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ESTIMATES OF WATER TRANSPORT PRODUCED BY WAVE ACTION

By

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The writer has received requests on several occasions to give estimates in concise form of the intensity of the transport of water caused by surface waves. It is hoped that the following discussion will be helpful in answering such questions, although it should be pointed out from the beginning that the actual conditions in the oceans depart very significantly from the ideal circumstances presupposed in the theory of the subject, so that great caution must be exercised in applying the theoretical results to practical problems in oceanography, pending comparison with observational data.[1]

[1] Under the actual circumstances in the oceans there are present such additional factors as the effect of the earth's rotation, pronounced irregularities in the waves themselves and, generally speaking, a certain horizontal stress at the surface due to the wind. It would therefore be of great interest to secure data on the actual transport produced by the waves in order to see whether, in spite of the added complexities, the simple theory here presented can be used at least as a first approximation.

In order to speculate concerning the possible state of affairs in an actual case, let us suppose that we are dealing with a large deep ocean which (for simplicity only) we assume to be free from permanent currents. Let us suppose further that there is present a steady and uniform wind which, after a suitable interval of time, establishes a stationary wave regime and also a system of steady drift currents near the surface. Since under these conditions it is necessary that the surface wind stress be exactly balanced by the Coriolis force associated with the momentum of the water, it follows that the *total* water transport must be at right angles to the stress. If there is to be

Dealing only with plane and periodic waves on the surface of a basin of very great depth, the instantaneous transport of mass across a fixed vertical plane normal to the direction of wave propagation (per unit distance along the crests) is given by

$$\int_{-\infty}^{z_0} \rho u dz \,. \tag{1}$$

Here z is the vertical co-ordinate counted positive upward, z_0 is the elevation of the free surface, ρ is the (constant and uniform) density and u is the x-component of the particle velocity. The x-axis is taken positive in the direction of wave propagation. If expression (1) is integrated with respect to time t over one wave period T, we obtain an expression for the net mass of water transferred, μ_t. Thus

$$\mu_t = \int_0^T \int_{-\infty}^{z_0} \rho u dz dt \,. \tag{2}$$

Since we assume that the waves move without alteration of their structure, it is possible to replace the time integration in (2) by a space integration over a wave length. Thus we shall employ the transformation

$$dx = cdt \,; \quad L = cT \,, \tag{3}$$

where c is the wave speed and L is the wave length, so that (2) becomes

$$\boxed{c\mu_t = m} \,. \tag{4}$$

In equation (4) m is the horizontal momentum per wave length. We thus see that *the horizontal momentum per wave length and per unit*

a component of this total transport in the direction of wave propagation, it would seem that the waves should run somewhat at an angle to the stress, a little to the right in the northern hemisphere and to the left in the southern. As an illustration, a wind of 15 m/sec would eventually establish waves which we might estimate to be 3 m in amplitude and to have a period of 13 sec. The same wind would produce a stress of about 7 dynes/cm^2 according to customary formulae. Computation shows that at middle latitudes the ratio of the wave transport to the total transport should be roughly about as 2 is to 7, so that the angle between the stress and the direction of wave propagation is 16 degrees. For the purpose of this illustration it has been assumed that the wave transport is given by Table I.

It is not clear, however, what the situation might be when waves are present but when the surface stress vanishes, since under such circumstances the total transport should also vanish.

TABLE I. Approximate Volume Transport Due to Surface Waves in Deep Water

(g = 980 cm per sec per sec)

				a = 0.5 m			a = 1.0 m			a = 2.0 m			a = 3.0 m			a = 4.0 m			a = 5.0 m			a = 6.0 m		
T	L	c	d	V_t	h	u_0	V_t	h	u_0	V_t	h	u_0	V_t	h	u_0	V_t	h	u_0	V_t	h	u_0	V_t	h	u_0
(sec)	(m)	(m per sec)	(m)	(m^3 per m per sec)	(cm)	(cm per sec)	(m^3 per m per sec)	(cm)	(cm per sec)	(m^3 per m per sec)	(cm)	(cm per sec)	(m^3 per m per sec)	(cm)	(cm per sec)	(m^3 per m per sec)	(cm)	(cm per sec)	(m^3 per m per sec)	(cm)	(cm per sec)	(m^3 per m per sec)	(cm)	(cm per sec)
3	14	04.7	01.1	0.26	05.6	23.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
4	25	06.2	02.0	0.20	03.1	09.9	0.79	12.6	39.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
5	39	07.8	03.1	0.16	02.0	05.1	0.63	08.1	20.2	2.51	32.2	81.0	—	—	—	—	—	—	—	—	—	—	—	—
6	56	09.4	04.5	0.13	01.4	02.9	0.52	05.6	11.7	2.09	22.4	46.9	4.71	50.4	105.5	—	—	—	—	—	—	—	—	—
7	76	10.9	06.1	0.11	01.0	01.8	0.45	04.1	07.4	1.80	16.4	29.5	4.04	37.0	66.4	7.18	65.8	118.1	—	—	—	—	—	—
8	100	12.5	07.9	0.10	00.8	01.2	0.39	03.1	04.9	1.57	12.6	19.8	3.53	28.3	44.5	6.28	50.4	79.1	9.82	78.7	123.6	—	—	—
9	126	14.0	10.1	0.09	00.6	00.9	0.35	02.5	03.5	1.40	09.9	13.9	3.14	22.4	31.2	5.59	39.8	55.6	8.73	62.2	86.8	12.57	89.5	125.0
10	156	15.6	12.4	0.08	00.5	00.6	0.31	02.0	02.5	1.26	08.1	10.1	2.83	18.1	22.8	5.03	32.2	40.5	7.85	50.4	63.3	11.31	72.5	91.1
11	189	17.2	15.0	0.07	00.4	00.5	0.29	01.7	01.9	1.14	06.7	07.6	2.57	15.0	17.1	4.57	26.6	30.4	7.14	41.6	47.5	10.28	59.9	68.5
12	225	18.7	17.9	0.07	00.3	00.4	0.26	01.4	01.5	1.05	05.6	05.9	2.36	12.6	13.2	4.19	22.4	23.4	6.54	35.0	36.6	9.42	50.4	52.7
13	264	20.3	21.0	0.06	00.3	00.3	0.24	01.2	01.2	0.97	04.8	04.6	2.17	10.7	10.4	3.87	19.1	18.4	6.04	29.8	28.8	9.00	42.9	41.5
14	306	21.8	24.3	0.06	00.3	00.2	0.22	01.0	00.9	0.90	04.1	03.7	2.02	09.2	08.3	3.59	16.4	14.8	5.61	25.7	23.1	8.08	37.0	33.2
15	351	23.4	27.9	0.05	00.2	00.2	0.21	00.9	00.7	0.84	03.6	03.0	1.88	08.1	06.7	3.35	14.3	12.0	5.24	22.4	18.7	7.54	32.2	27.0
16	399	25.0	31.8	0.05	00.2	00.2	0.20	00.8	00.6	0.79	03.1	02.5	1.77	07.1	05.6	3.14	12.6	09.9	4.91	19.7	15.4	7.07	28.3	22.2
17	451	26.5	35.9	0.05	00.2	00.1	0.19	00.7	00.5	0.74	02.8	02.1	1.66	06.3	04.6	2.96	11.2	08.2	4.62	17.4	12.9	6.65	25.1	18.5
18	505	28.1	40.2	0.04	00.2	00.1	0.17	00.6	00.4	0.70	02.5	01.7	1.57	05.6	03.9	2.79	09.9	06.9	4.36	15.5	10.9	6.28	22.4	15.6
19	563	29.6	44.8	0.04	00.1	00.1	0.17	00.6	00.4	0.66	02.2	01.5	1.49	05.0	03.3	2.65	08.9	05.9	4.14	13.9	09.2	5.95	20.1	13.3
20	624	31.2	49.6	0.04	00.1	00.1	0.16	00.5	00.3	0.63	02.0	01.3	1.41	04.5	02.8	2.51	08.1	05.1	3.93	12.6	07.9	5.65	18.1	11.4

distance along the crests is equal to the wave speed multiplied by the mass of water transported during one wave period per unit distance along the crests. The momentum per wave length is thus the same as that of a mass of water μ_t moving with the wave speed.

In papers published previously by the writer (Starr, 1947a, b), attention was called to a relationship originally established by Levi-Civita, namely that for periodic waves in an irrotational medium,

$$cm = 2e \; ; \left(e = \int_0^L \int_{-\infty}^{z_0} \rho \frac{u^2 + w^2}{2} \, dz dx \right), \tag{5}$$

where w is the vertical component of the particle velocity, so that e is the kinetic energy per wave length and per unit distance along the crests. Elimination of m between (4) and (5) yields the equation

$$\boxed{e = \tfrac{1}{2} u_t c^2} \; . \tag{6}$$

Thus the kinetic energy per wave length and per unit distance along the crests is equal to one half the mass transported per wave period and per unit distance along the crests, multiplied by the square of the speed of propagation. The kinetic energy per wave length is thus the same as that of a mass of water μ_t moving with the wave speed.[2]

In order to provide a means readily grasped by the imagination for representing some of the concepts discussed above, let us suppose that a mass of water μ_t per wave length is spread horizontally in the x-direction so as to form a layer of uniform thickness h. It follows that

$$h = \frac{\mu_t}{\rho L} \; . \tag{7}$$

If v is the potential energy of the actual waves per wave length (and per unit distance along the crests), this energy is equivalent to the work done in lifting the layer h through an appropriate vertical distance d. If, in addition, we impart a uniform horizontal translation to the layer h, equal to the wave speed c, the following statements are true:

(1) The average potential energy of the waves per unit area of sea surface is equal to the work done per unit area in lifting the layer h through a vertical distance

[2] In the papers by the writer already alluded to, it was shown that an equation of the same form as (5) is valid not only for the entire depth of the water, but also for any material layer bounded above and below by streamlines for the motion relative to the moving wave. It remains to be pointed out that an equation of the form (4), and consequently also one of from (6), is also valid for such a material layer.

$$d = \frac{v}{g\rho hL} = \frac{v}{g\mu_t}, \tag{8}$$

where g is the acceleration of gravity.

(2) The average volume transport per unit time and per unit distance along the crests is the same as that of the layer h, namely,

$$V_t = ch = \frac{c\mu_t}{\rho L}. \tag{9}$$

(3) The average horizontal wave momentum per unit area of the sea surface is the same as the horizontal momentum of the layer h per unit area, namely,

$$\frac{m}{L} = \rho ch = \frac{c\mu_t}{L}. \tag{10}$$

(4) The average kinetic energy per unit area of the sea surface is the same as the kinetic energy per unit area of the layer h, namely,

$$\frac{e}{L} = \tfrac{1}{2}\rho hc^2 = \frac{c^2\mu_t}{2L}. \tag{11}$$

It is, however, important to observe that the layer h cannot serve as a dynamic substitute for the wave motion in certain other ways. In particular it is especially important to note that in the layer h the transport of kinetic plus potential energy during one wave period is equal to $e + v$, whereas in the actual wave motion it is generally recognized that this transport is about one half as great, at least as a first approximation.

The material presented above is independent of any restriction to small amplitudes. However, in order to present some idea of actual magnitudes in specific cases we shall now use certain approximate expressions derived from the small-amplitude theory. These are that

$$e = v = \tfrac{1}{4} g\rho a^2 L, \tag{12}$$

$$c^2 = \frac{gL}{2\pi}, \tag{13}$$

where a is the amplitude of the waves at the free surface which is assumed to be of sinusoidal form. From (6), (12) and (13) it follows that

$$\mu_t = \pi\rho a^2. \tag{14}$$

From (7) and (14) it follows that

$$h = \frac{\pi a^2}{L}. \tag{15}$$

From (8), (12) and (14) it follows that

$$d = \frac{L}{4\pi}. \tag{16}$$

From (3), (9) and (14) it follows that

$$V_t = \frac{\pi a^2}{T}. \tag{17}$$

Numerical values of c, T, d, h and V_t are given in Table I, together with u_0 the surface particle transport velocity for various values of amplitude and wave length. The surface particle transport velocity is calculated by means of an approximate formula[3] given by Lamb (1932), namely,

$$\frac{4\pi^2 a^2 c}{L^2} exp \frac{4\pi}{L} z. \tag{18}$$

APPENDIX

Although it may seem somewhat surprising that the surface wave problem is characterized by three exact relationships as simple as (4), (5) and (6), still it might have been anticipated purely on *a priori* grounds that equations of this form should exist, provided that the present subject is brought into proper relation with another topic in classical hydrodynamics. The writer has in mind the theory of the motion of a solid through an infinite liquid, according to which the solid in certain cases reacts to the action of an external force in a manner as though its inertia were artificially increased by a constant amount depending upon the configuration of the solid and the direction of the applied force. For a discussion of this theory the reader is referred to Lamb (1932).

In order to apply the principle to the wave problem, let us consider an admittedly artificial but nevertheless theoretically satisfactory mode of generating surface waves of a given wave length and height. We shall suppose that we have at our disposal a rigid corrugated metal sheet of negligible mass per wave length, having the precise shape of the profile of the waves to be generated and also having a large number of wave lengths. We may suppose that the waves are to be generated

[3] This formula was obtained through the use of the second-order approximation to the solution of the wave problem. It is to be noted that when integrated it gives a result in agreement with (17). Mr. G. W. Platzman has informed the writer that he has carried out a computation of the transport velocity which includes terms of the eighth order. From his results it appears that, for waves of the extreme form, the surface transport velocity is equal to about one fifth of the wave speed.

in a canal of great depth but of unit width. If the sheet is placed on the surface of the water in such a way that no space remains between it and the water, an amount of work equal to v will have been done per wave length in producing the deformations.

Let us suppose next that, with the sheet constrained to move horizontally, a certain constant arbitrary force f per wave length is applied horizontally to the sheet. The effect will be to accelerate the sheet until after some appropriate time t_1 it will be moving with the velocity c, the (predetermined) wave speed corresponding to the chosen wave length and wave height. At this time the force f may be discontinued and the sheet removed.

The process which has taken place may be analyzed as follows. Assuming that, with the sheet in place at time $t = o$, the water is at rest, all the motions subsequently generated are irrotational and hence determined completely by the motion of the boundary. Except for end effects which become of negligible importance if a very large number of wave lengths are used, at time $t = t_1$ the motion of the boundary is the same as the motion of the geometric curve representing the moving profile of the desired waves, hence the particle motions must be those corresponding to the desired waves and the dynamic reactions of these motions will produce a constant pressure at the upper boundary as is needed. If the force f is taken very large, in the limit the motions may be considered as being started instantaneously by impulsive action, although it will be more convenient to suppose that the process takes place during a finite time interval.

At this point an assumption must be made which however seems reasonable. The sheet used, instead of being immersed in fluid, is in contact with water only on the lower side. Since, in the limit when the number of wave lengths used is very large, the two regions above and below are independent of each other, we shall assume that the artificial mass of the sheet is simply some fraction of what it would be in the case of immersion. Actually the presence of the artificial inertia is due to the fact that as the solid object is accelerated certain motions must be generated in the fluid. In our case the motions generated in the water are known to be periodic in the x-direction so that the artificial mass must be regularly distributed along the sheet. Without making any supposition as to magnitude, we thus assume that this virtual mass is an amount μ_i per wave length and proceed to write an equation of motion for it, namely,

$$\mu_i \frac{d^2x}{dt^2} = f. \tag{19}$$

Since μ_t is a constant determined by the shape of the sheet, a single integration gives

$$\mu_t \frac{dx}{dt} = ft \; ; \quad \left(\frac{dx}{dt} = 0 \; for \; t = 0\right). \tag{20}$$

For time $t = t_1$, $dx/dt = c$ and $ft = m$, so that $c\mu_t = m$, which is (4). A second integration gives

$$\mu_t(x - x_0) = \tfrac{1}{2} ft^2 \; ; \; (x = x_0 \, for \, t = 0) \, . \tag{21}$$

For time $t = t_1$, the quantity $f(x - x_0)$ is the work done, which must be equal to e the added energy, so that, with the aid of (20),

$$e = f(x_1 - x_0) = \tfrac{1}{2} \frac{f^2 t_1^2}{\mu_t} = \tfrac{1}{2} \mu_t c^2 \, , \tag{22}$$

which is (6). Elimination of μ_t between (4) and (6) finally gives (5).

The writer wishes to express his thanks to Mr. G. W. Platzman for reading the manuscript.

SUMMARY

In this paper it is shown that for periodic surface gravity waves in a basin of great depth there exists a theoretical integral relationship according to which the horizontal momentum per wave length and per unit distance along the crests is equal to the wave speed multiplied by the mass of water transported horizontally during one wave period per unit distance along the crests. It is also shown that, in the case of irrotational waves, the kinetic energy per wave length and per unit distance along the crests is equal to one half the mass of water transported per wave period and per unit distance along the crests, multiplied by the square of the speed of propagation. An attempt is made to explain the existence of these relationships, as well as the existence of another similar integral discussed by the writer previously, by bringing the surface-wave problem under the general scope of the classical theory of the motions of solids through liquids.

The various concepts arising in the discussion are illustrated by means of a simple dynamic analogue consisting of a plane horizontal sheet of water moving with the wave speed and having the same potential energy, mass transport, and kinetic energy as the actual wave motion. A table giving the magnitude of the water transport in specific cases is included. This table was prepared with the aid of the small-amplitude theory of gravity waves.

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DEEP SEA PHOTOGRAPHY

By

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Interest of the senior author in deep sea photography stems from a desire to obtain photographs of deep sea luminous fish—not by their own light, but in their natural environment, using artificial illumination. The abundance of deep sea forms observed by Beebe (1934) from his bathysphere suggests that success might be achieved, especially if a lure could be found that would attract deep sea fish to the front of the camera.

Just before the war, a pressure chamber was designed (Harvey, 1939) and manufactured[1] that would withstand two miles of depth in the sea with a considerable safety factor. In this chamber, shown in Fig. 1, two six-volt storage batteries supplied the current to run the motor for a 16 mm. moving picture camera, a 50 candle power headlight bulb with reflector, and a timing motor. The light shone through one "herculite" glass window, while the camera took pictures through another. Anhydrous $CaCl_2$ prevented moisture condensation on the glass. A pressure gauge with electric contacts, which could be set for any depth, activated the mechanism by means of a lock relay. This relay started the timing motor, whose contacts turned on the movie camera and light for 1.2 seconds and then turned them off for 11.1 seconds, when the process was repeated. The camera was set to take 16 pictures a second, and the films when developed showed a series of 20 exposed frames between 3 dark ones, since the lamp filament took some time to reach incandescence and the motor some time to stop. In 100 feet of film with 40 frames per foot, there were about 170 chances of photographing something, and 3,400 exposures. Since the pictures were taken in the zone of perpetual darkness, a lure was hung four feet in front of the pressure chamber, and the camera (with stop f 1.5) focused on it. This lure was a wooden fish resembling a deep-sea fish, with rows of photophores painted on it with self-luminous zinc sulfide paint.

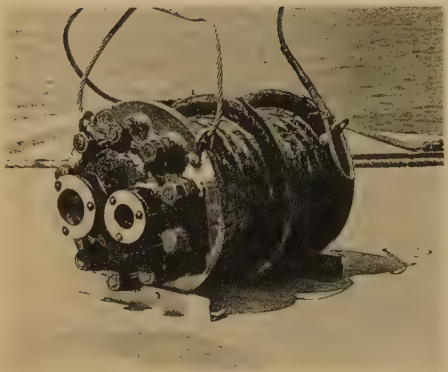
[1] The chamber was made by the Springfield Boiler Co. and was a gift of its President, Mr. Owsley Brown.

In all, seven descents[2] were successfully accomplished with this camera. Five of them took place in the region 5 to 10 miles southeast of Bermuda, where Beebe had made over 1,500 hauls with nets and many descents with the bathysphere. Three 100-ft. rolls of super XX panchromatic film were taken at 500 fathoms, one at 800 fathoms, and one at 1,320 fathoms (1½ miles). In the latter, the chamber touched bottom, knocking off a support and turning the camera out of position so that nothing appeared on this film. The other four films showed the lure clearly, but no fish or large organisms. However, 17 small organisms, the largest about one centimeter in diameter, too small to be identified, moved across the beam of light in the 300 feet of film taken at 500 fathoms, the depth where Beebe obtained most material in his hauls with the nets. The film at 700 fathoms showed only two small creatures.

Two other successful tests were made from the "Atlantis" about 500 fathoms down in the Atlantic Ocean, south and east of Boston. About 23 small organisms appeared on these two 100-foot films. Thus 600 feet of film, representing 1,020 chances of photographing something and 20,400 individual frames, revealed only 42 small organisms and no fish the size of deep sea types. The chief conclusion to be drawn from this summer's work is that deep nekton fish are not abundant and not attracted to the luminous lure that was used. Perhaps they are frightened away by the sound of the motors within the chamber.

During the war, photography of the sea bottom was carried to a high degree of perfection by Ewing, Vine and Worzel (1946), and Ewing, Woollard, Vine and Worzel (1946). The published photographs of this group are beautifully clear and some of their unpublished photographs of deep sea-bottom invertebrates are truly remarkable. These authors used a small camera (in a pressure chamber) that took single or two successive pictures, with photoflash bulbs for illumination. In their arrangement, the camera chamber and photoflash lighting are separate and fastened on a pole, held vertical by a float. In one type (the free floating camera), a ballast weight is released after the outfit has touched bottom and the exposures have been made by means of a trigger that actuates clockwork, opening the shutter and firing the photoflash bulbs. The camera then rises to the surface to be retrieved and reset. In a second type (the suspended camera), the camera and flash lights are arranged on a vertical pole as in the first type, but the assembly is

[2] Five tests of the camera were made through the kindness of Dr. J. F. G. Wheeler, Director of the Bermuda Biological Station in 1939, from the ketch "Culver," permanently stationed in Bermuda for oceanographic work. Later, in July and August, two more tests were made from the ketch "Atlantis," through the kindness of the Director of the Woods Hole Oceanographic Institution, Dr. Columbus Iselin.



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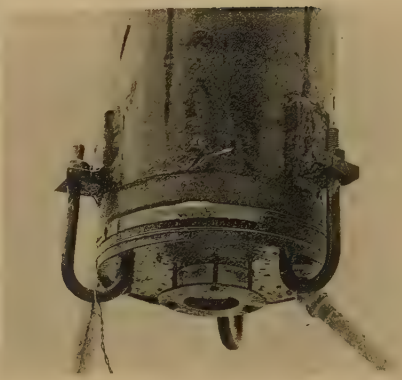

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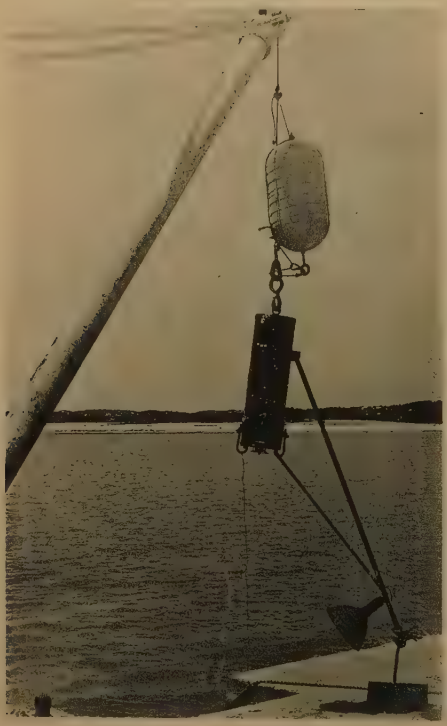

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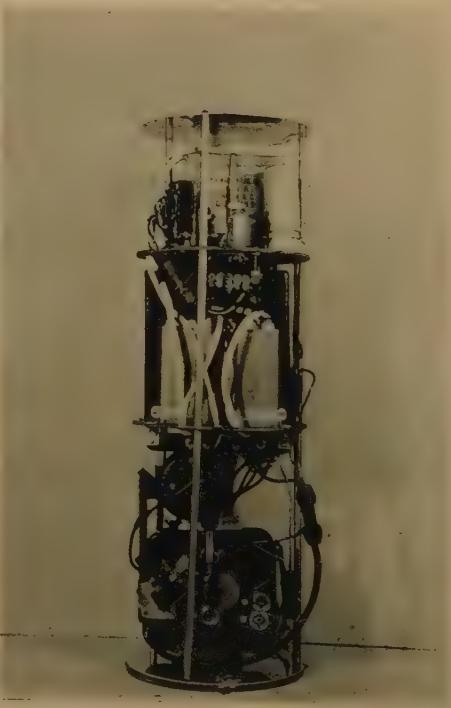

D

Figure 1

A. Front view of the 1939 deep sea camera chamber, showing cover with large glass window through which an incandescent bulb illuminates the region of the lure and the small glass window through which motion pictures are taken.

B. The black cylindrical pressure chamber of the 1946 deep sea camera hung from a boom, with attached float (above) and ballast weight and light (below). The rectangular ballast, attached to a pipe screwed into one of three brackets near the upper end of the pressure chamber, rests on the pier. The reflector and the flash tube are just above the ballast. Making a right angle at the end of the flash tube chamber is a pipe containing wires for the high voltage impulse generated within the main pressure chamber. This pipe enters the chamber through the cover. The float is an airplane oxygen tank filled with compressed air. Its purpose is to keep the whole outfit in a vertical position, without lifting it off the bottom. For a long series of pictures, the camera assembly can be attached by a cable to another float at the surface, thus recording the succession of animal events during a whole night.

Two additional brackets (not shown in picture) take two additional pipes to form a tripod, when the chamber is to be used resting on the bottom without a float. For deep sea photography above the bottom, float and ballast weight are removed.

C. Near view of the cover end of the chamber, with "Herculite" glass window held in place by a metal disk. The cover fits in smoothly machined grooves, and is held tight by three dogs. A heavy rubber band covers the joint and is squeezed tight by wire rings. As the hydrostatic pressure increases with depth the rubber band is pressed firmly on the cover-chamber joint, preventing leakage into the chamber.

D. A photograph of the internal mechanism, showing distribution of contents in three compartments. In the lower compartment are relays and clock timer (not visible in photograph), camera and motor, and the connections for wires to the flash lamp. In the middle compartment are the high voltage condenser and storage battery. In the upper compartment are transformers, interrupter, capacitances, resistors and a rectifier for generating the high voltage pulse to the flash tube.

suspended from a cable. When bottom is touched, a trigger actuates the exposures and the instrument is then drawn to the surface. The many interesting snapshots obtained with the above types of camera indicate that life on the ocean bottom is remarkably rich.

The problem of photographing deep sea fish which live well above the bottom is one involving (1) attraction of the fish and (2) a succession of rapid exposures, to increase the chance of photographing something. The situation is comparable to a photographer who aims his camera skyward at random, hoping to photograph a bird; the bird must be lured near the camera by some device. Unfortunately we know nothing of the objects likely to attract a deep sea fish and can only surmise that, unlike surface fish, they would avoid a bright steady light but be attracted to the kind of luminous lure that most nearly resembles their own pattern of photophores. Perhaps some kind of bait should be used.

With these thoughts in mind, we designed a new type of deep sea camera, self contained in all particulars, that can be lowered to depths of one half mile, the region of maximum concentration of deep sea organisms. Weight was reduced as much as possible, so that the outfit could be handled from a relatively small laboratory launch.

In the new design, the camera was an old but compact Zeiss Ikon Universal Kinamo for motion pictures, with f2.5 tessar lens, holding about 40 feet of 35 mm film, and driven by a 12 volt D. C. motor (with reducing gears) at a slow speed of one frame every five seconds. The shutter was removed from the camera and a commutator placed in the driving mechanism, to trigger a G. E. FT-10 flash tube by means of a microswitch contact every five seconds. Current from a 28 microfarad condenser, charged to about 2,000 volts, passing through the flash tube gave the illumination for instantaneous photography, with exposures of nine microseconds, sufficient to obtain clear pictures of any fish, no matter how rapid its movement.

The camera, mounted behind a herculite glass window, the motor, storage battery, relays, condensers, interrupters, and other parts of the flash tube circuit[3] were placed in a ¼″ thick steel tube, 8″ inside diameter and 25″ long, with heavy steel ends. The flash tube and trigger coil were contained in a second smaller steel chamber with a thick glass bowl on one end through which the light of the flash was directed toward objects in front of the camera. A reflector helped

[3] For the design and construction of the lighting circuit we are deeply indebted to Dr. H. E. Edgerton of the Massachusetts Institute of Technology. Thanks are also due to Mr. Harold Towne, technical assistant to Dr. Harvey, for skillful installation in the limited space of the chamber, and to Mr. Russell Mycock for machining the steel parts.

concentrate the light. Insulated wire connections between the light chamber and the main pressure chamber were made through a well braced steel pipe that also served to hold the light three feet away from the main chamber and at a 45° angle with the axis of photography. A bait or lure could be dangled before the chamber and the camera focused on it. The complete outfit weighed about 150 pounds. It is pictured with the internal mechanism in Fig. 1.

The deep sea camera could be used either (1) free, suspended from a cable at various depths, or (2) attached to a tripod so as to rest five feet above the bottom, or (3) held by a weight and float at a distance of five feet from the bottom. The camera and lighting mechanism could be started either after a given time interval, by a clock and contact within the chamber, or, by a pressure gauge and contact after a certain depth had been reached.

The camera assembly was tested during the summer of 1947 at the Bermuda Biological Laboratory[4] and proved to be a practical tool that could be handled from the 28-foot laboratory launch "Diadema," equipped with an aircraft bomb lifting winch and one eight-inch stranded steel cable. An unfortunate accident, the result of acid leaking from the storage battery, ruined the camera and prevented its use at depths of one half mile, but pictures of the bottom and of coral heads and sea weed were obtained at moderate depths. However, no living animals appeared within the field of view in over a thousand individual photographs. It is possible that the succession of flashes every five seconds actually scares animals away, an important point that should be determined for shallow water fish, where effects of the flashing light can be observed. Whether deep sea fish, whose reactions to bright lights are unknown, would behave in the same way, is another question.

The flash of light is extraordinarily bright and can be seen under water at night for long distances. In future modifications, it would probably be better to increase the interval between exposures from five seconds to one minute or perhaps more, in order to allow animals to recover from the previous flash. Dry batteries might be substituted for a storage battery or the latter placed outside the pressure chamber. With such an outfit it is believed that many problems connected with the behavior of deep sea fish might be solved.

[4] The authors express their thanks for the facilities of the Bermuda Biological Station and their appreciation of the advice and co-operation of its Director, Dr. Dugald E. S. Brown.

SUMMARY

A new type of camera, in a pressure chamber, and its lighting mechanism, is described for photographing organisms in the depths of the sea. Six hundred and forty pictures, at intervals of five seconds or more, can be taken on 35 mm film before reloading. Discharge of a condenser through a flash tube is used for lighting; the exposure is about 10 millionths of a second. The total weight for depths of one half mile is about 150 pounds; for greater depths thicker walls and more weight is necessary. Some of the necessities for successful photography of deep sea luminous fish are discussed.

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UNUSUAL PHOSPHORUS CONCENTRATIONS IN THE FLORIDA "RED TIDE" SEA WATER

By

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Beginning in late November 1946, and continuing at sporadic intervals until July 1947, a flowering of *Gymnodinium* sp. caused discolored water off the west coast of Florida. Millions of fish were killed along the coastline and this mortality was always directly associated with the presence of *Gymnodinium* (Gunter, Smith and Williams, 1947). The phenomenon has been popularly called the "Red Tide."

Under normal conditions in the sea, phytoplankton production is limited by the supply of phosphorus and nitrogen compounds. It was thought pertinent to inquire whether the tremendous populations of *Gymnodinium* observed were able to exist with the normal nutrient supply of the sea or whether additional supplies of nutrients had become available in some way to support this flowering.

Between July 22 and 24, when an intense flowering was under way near Sarasota, Florida, various water samples were obtained by Mr. William Anderson for Dr. Paul Galtsoff, U. S. Fish and Wildlife Service. These samples were preserved with chloroform and were made available for determination of total phosphorus content. Similar samples taken one month later, during a period when there was no evidence of the plankton bloom, were also analyzed for comparison.

The total phosphorus was determined by the method described by Redfield, Smith and Ketchum (1937). The results include the organic phosphorus combined in particulate matter and plankton, the organic phosphorus in solution in the water, and inorganic phosphate-phosphorus. In different stages of the cycle of synthesis and decomposition of organic matter in the sea the proportion of phosphorus in each of these fractions will differ greatly (Ketchum, 1947). The inorganic phosphorus, which is available for assimilation by the plankton, was found by Dr. R. H. Williams[2] to be undetectable in an area NE. of Key West shortly after a heavy outbreak of the Red Tide. Apparently it was all combined in one or the other of the organic fractions.

[1] Contribution No. 419 from the Woods Hole Oceanographic Institution.

[2] Personal communication.

Since our analyses include all organic and inorganic phosphorus compounds in the water, they indicate the total amount of phosphorus which had been available for synthesis into organic matter. The maximum concentration of phosphorus to be expected in the sea is about 2.0 microgram atoms per liter (Sverdrup, Johnson and Fleming, 1942).

TABLE I.—Total Phosphorus Content of Water

Samples Taken Off Florida Coast During and After the Flowering of *Gymnodinium* Sp. (Red Tide).

Location and Condition of Water in July	*July, 1947*		*August 22, 1947*	
	Salinity °/₀₀	*Total P.* μg. at./L.	*Salinity* °/₀₀	*Total P.* μg. at./L.
A. 5 mi. off Sarasota Point; 50 yards outside amber water.	32.9	2.48	33.4	0.81
In water of deep amber color.	33.2	20.4	—	—
B. 3½ mi. off Sarasota Point; water, deep amber color.	32.5	8.80	33.6	1.00
C. 1 mi. south of Sarasota Point; water, light amber color.	33.2	4.92	32.9	1.22
D. 1½ mi. off Sarasota Beach and 1½ mi. above Pt. O'Rocks; water, deep amber color.	32.5	14.6	33.2	1.08
E. 3 mi. off Musketeer's Pass; water, deep amber color.	33.2	5.96	33.6	0.62
F. 3 mi. up from Venice Inlet ½ mi. off beach, in clear blue water.	33.2	1.15	—	—

The locations of the collections are shown in Fig. 2 and the results of the analyses in Table I. In July the samples of water taken outside the discolored area contained normal phosphorus concentrations. Within the discolored area, however, the total phosphorus content varied from 4.9 to 20.4 microgram atoms per liter. This is approximately 2½ to 10 times the normal expected concentration. The samples taken in the same places in August contained between 0.62 and 1.22 microgram atoms per liter and were, consequently, all within the range to be expected in sea water. The salinity data indicate that there was little difference in the amount of fresh water present at the times of sampling. According to Parr (1935) the salinity of the offshore water in this area is about 36°/₀₀. These water samples, therefore, contained no more than 10% fresh water derived from rain and drainage.

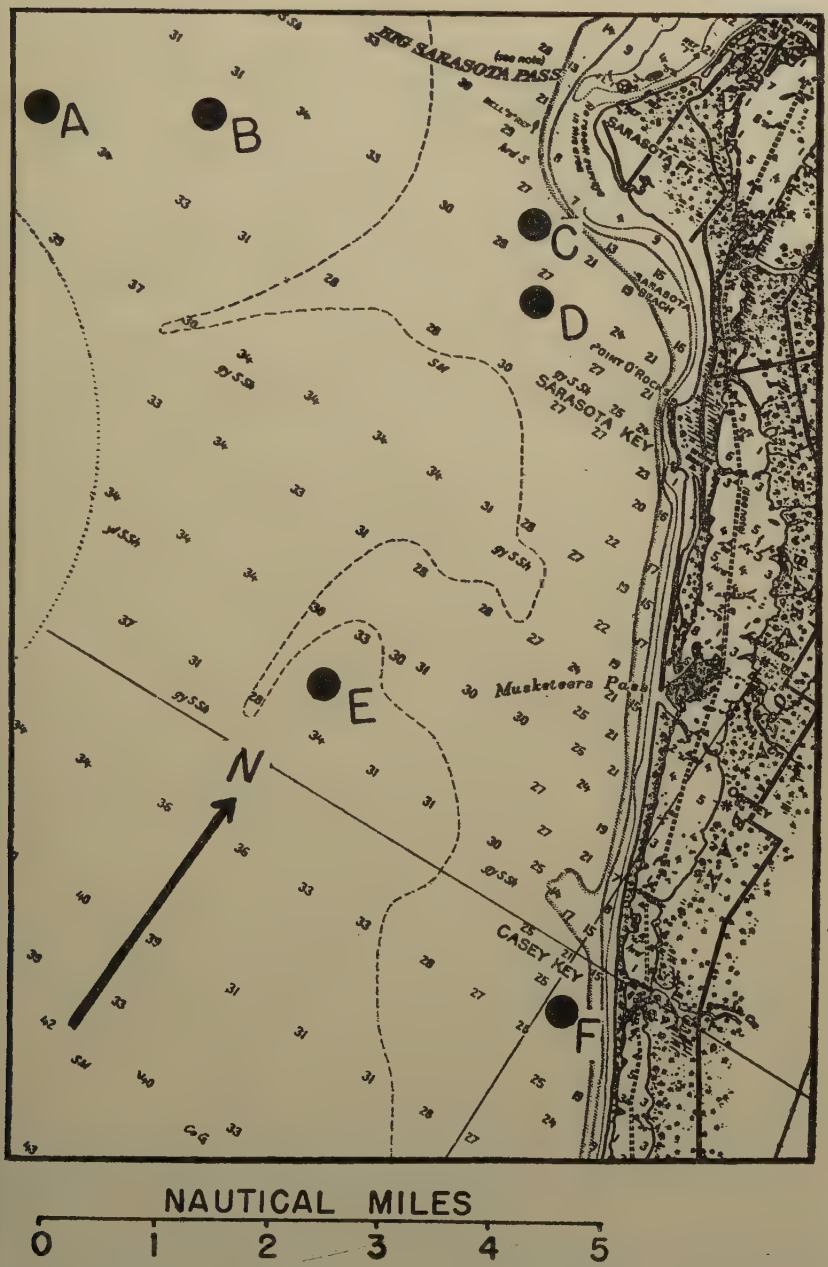

Figure 2. Section of chart off Sarasota, Florida, showing locations where water samples were taken. The depths are in feet at mean low water.

Discussion

The available data on the distribution of phosphate-phosphorus in this general area are meagre. Riley (1937, 1938) and Rakestraw and Smith (1937) found surface concentrations of 0.02–0.5 microgram atoms per liter in this general area and in the Caribbean. The latter authors found maximum values of 2.0 microgram atoms per liter at depths of 500–2000 meters. The water which supported the large populations of *Gymnodinium* thus contained more phosphorus than is present in any of the major water masses of the area. This fact excludes the possibility that the flowering can be attributed to the upwelling of nutrient-rich, deep water from the mid-Gulf.

Two processes which might explain such high concentrations of phosphorus may be postulated. The excessive nutrient content may be the result of terrigenous contamination or fertilization of the waters, or it may be the result of active swarming of the organisms.

If it is the result of terrigenous contamination, an enormous quantity of phosphorus must be contributed to account for the extent of the flowering. The water in this area is on the average 10 meters deep. If the phosphorus is uniformly distributed to this depth, an average total of 3–6 grams per square meter of sea surface would be present. The addition of 3 grams of phosphorus per square meter would require about 17,000 pounds of pure phosphorus per square mile (*i. e.*, about 340,000 pounds of "Superphosphate" fertilizer containing 5% P). The reports of the extent of the flowering indicate that areas of several square miles were affected. The salinity data show that there was little or no excess fresh water drainage in the July samples, and it seems unlikely that the drainage water would vary so tremendously in its phosphorus content. Therefore, the possibility that water-borne contamination has caused these results seems unlikely.

It is conceivable that the *Gymnodinium* could assimilate all of the phosphorus of the water column and subsequently swarm at the surface, thus giving rise to the observed high concentrations. Using again the average depth of 10 meters, if all of the phosphorus were concentrated in a surface layer one meter deep, a tenfold increase would thus be accounted for. The *Gymnodinium* cells have been observed to accumulate at the surface of jars of sea water collected from the affected area. Such accumulation in the open sea, however, would require very calm conditions so that the mixing of the water and the resultant downward transport of the cells would be at a minimum.

To differentiate between these two possibilities, water samples from various depths in the affected areas should be analyzed. External contamination would be indicated if the total phosphorus content of the water column were greater than would be expected from the

normal content of the sea. The distribution and source of this contamination could be traced easily by the proper spacing of sampling locations. Determination of the carbon: nitrogen: phosphorus ratios of the plankton cells would show whether phosphorus alone or a "balanced fertilizer" had been the contaminant. On the other hand, if most or all of the phosphorus of the water column were concentrated in the surface layers, swarming of the *Gymnodinium* cells would be suspected. This note is presented in the hope that future investigation of similar phenomena will give an answer to this problem.

Summary

1. The total phosphorus content of waters containing dense *Gymnodinium* populations was found to be 2½ to 10 times the maximum to be expected in the sea. The possibility that upwelling of nutrient-rich, deep water is the explanation of this intense plankton bloom is thereby excluded.

2. It is suggested that future studies of intense plankton blooms include total phosphorus determinations at various depths. The results would differentiate between terrigenous contamination and swarming of the organisms at the sea surface.

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ARSENIC IN THE SEA[1]

By

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Although the microdetermination of arsenic in biological materials is of interest because of its toxicity, still the determination of arsenic in sea water has received but little attention, despite the fact that most of the marine animals and plants concentrate this element in their tissues. We are in some doubt about the physiological significance of arsenic, as well as about the forms in which it occurs in the sea.

The arsenic content of sea water has been investigated by Gautier (1903), who found about 10 mg./m³., and by Rakestraw and Lutz (1933), who found 9 to 22 mg./m³. Fedossov (1940) investigated the arsenic content of the Azov, Black and Caspian Seas, and found 5.7, 10 and 6 mg./m³., respectively.

Methods. Several methods have been used for the microdetermination of arsenic, but most of these are either not sensitive enough (as the Denigès, Reinch and titration methods), sensitive but not successful for quantitative estimation (as the Bettendorf method), or laborious and cumbersome (as the Marsh method).

In general, these procedures depend upon the separation of arsenic in some form. For example, arsenic is distilled as $AsCl_3$, and then titrated. In the Gutzeit process it is liberated in the form of arsine, AsH_3, which is made to react and produce a stain on $HgBr_2$ paper. Consistent results in the latter case can only be obtained after considerable experience. Nevertheless, this method is still widely used because of its simplicity. Certain modifications in the Gutzeit process have been proposed, such as the replacement of paper strips by paper discs or thread, or the use of constant-area zinc pellets for the generation of hydrogen at a constant rate. The method used in this study is essentially that of Jacobs and Nagler (1942).

Apparatus. The apparatus (Fig. 3) consists of the usual Gutzeit generator, a tube to remove impurities, and an absorption tube filled

[1] Contributions from the Scripps Institution of Oceanography, New Series, No. 360.

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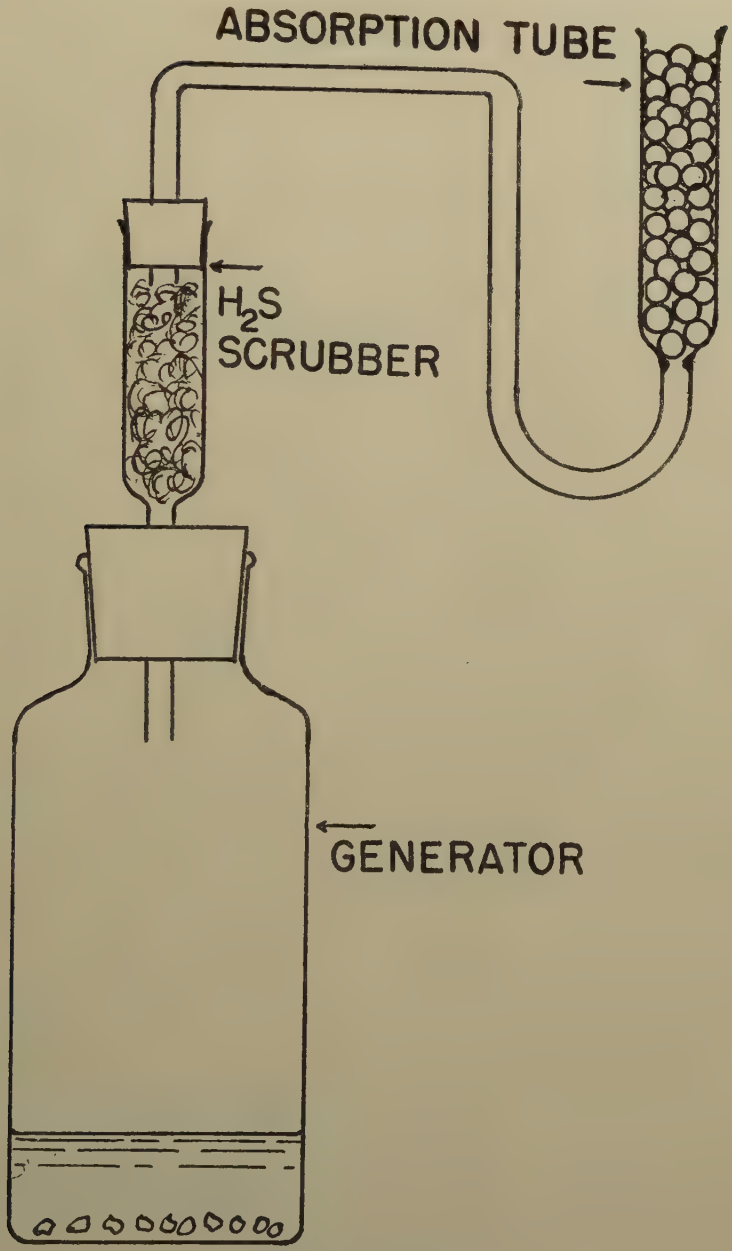

Figure 3. Apparatus.

with glass beads and NaOBr solution, in which the arsine is taken up and oxidized.

Reagents. Sodium Hypobromite Solution. The stock (saturated) solution consists of 2 ml. of bromine in water. For use, this is diluted with an equal volume of water, and to the half-saturated solution is added 0.5-*N* NaOH in the proportion of 1 : 3.

Ammonium Molybdate Solution: Dissolve 25 g. of ammonium molybdate in 300 ml. of water. Dilute 75 g. of concentrated H_2SO_4 to 200 ml. with water and add it to the ammonium molybdate solution.

Standard Arsenious Oxide: Dissolve 0.300 g. As_2O_3 in 25 ml. of 10% NaOH. Make slightly acid with H_2SO_4 (1 : 6) and dilute with water to one liter. Five ml. of this stock solution diluted to one liter gives a solution containing 1.5 μg. of As_2O_3 per ml.

Hydrazine Sulfate Solution: Dilute a saturated solution with water (1 : 1).

Sulfuric Acid Solution: 2-*N* prepared and standardized in the usual way.

Stannous Chloride: Dissolve 40 g. $SnCl_2.5H_2O$ in 100 ml. HCl (sp. g. 1.184).

Zinc: Both 30-mesh C. P. granulated zinc and C. P. zinc shot were used. The former needed no activation and gave low recoveries of arsenic. Zinc shot, however, was activated by HCl (1 : 3), to which 2 ml. of $SnCl_2$ solution was added.

Method. To the sample[3] were added 4 ml. of concentrated HCl, 2 ml. of concentrated H_2SO_4, and 10 to 15 g. of activated zinc shot. Three ml. of NaOBr solution was put in the absorption tube. The generator was immersed in a water bath at 20–25° C. to insure an even rate of hydrogen evolution, and the gases were allowed to evolve for at least two hours. The time and rate of hydrogen evolution are exceedingly important and experience is necessary to insure complete recovery of arsenic.

The NaOBr solution was then transferred to a 25-ml. glass-stoppered measuring cylinder. The tube was washed with six 2-ml. portions of distilled water. Five ml. of 2-*N* H_2SO_4, one ml. of ammonium molybdate reagent, and one ml. of hydrazine sulfate solution were added and the total volume made up to 25 ml. with water. The color was allowed to develop for one-half hour, after which it was measured in the spectrophotometer. (A Bausch and Lomb instrument was used.)

Eighteen standard solutions were prepared, containing from 9.75 to

[3] At least 500 ml. of the water is evaporated down to a quantity suitable for use in the generator. Separation of solid is not disturbing.

40 mg. of As_2O_3 per cubic meter. These were put through the foregoing procedure and the spectrophotometer readings (d) were plotted against As concentration. A linear relation was found from which all subsequent values were derived.

The maximum absorption of the color of the reduced arsenomolybdic acid is known to be in the infrared at a wavelength of 840 millimicrons. Since this range is invisible to the human eye, the nearest and clearest band was found to be at 700 millimicrons, which was used for all the readings.

The blank had an almost imperceptible greenish blue color which, when measured against pure distilled water, gave a density reading of 0.08. The blank was used in the spectrophotometer as the comparison liquid.

The modified Gutzeit procedure just described will determine only arsenite, or trivalent arsenic (As^{III}). It is necessary to reduce arsenate, or pentavalent arsenic (As^{V}) before it can be determined by this method.

Solutions were prepared containing varying amounts of As^{III} and As^{V} in 1.9% NaCl solution and three methods of reduction were tried, as follows:

(a) After adding 0.5 ml. of 3-*N* H_2SO_4 and 0.4 g. of $NaHSO_3$, the solution was heated to 70° C. for 60 minutes, followed by two minutes of boiling to remove SO_2.

(b) Boiling for three minutes after adding one ml. of 50% KI solution and one ml. of 40% $SnCl_2$ solution (in conc. HCl).

(c) Boiling for two minutes after adding 2 ml. of a solution of 17 g. KCl, 4 g. KBr and 5 g. hydrazine sulfate in 100 ml.

From Table I, which shows the results in terms of arsenic added and recovered, it may be seen that method (a) is the most satisfactory.

TABLE I.—Effectiveness of Different Methods for Reduction of Arsenate (As^{V})

Arsenic added (μg.)			*Recovered by reduction method* (μg.)		
As^{III}	As^{V}	*Total*	(*a*)	(*b*)	(*c*)
—	20	20	20.5	8.0	10.0
5	15	20	21.0	10.5	13.5
10	10	20	19.5	15.0	14.0
15	5	20	20.0	16.5	19.0

Total Arsenic. For the determination of total arsenic, both inorganic and organic, a method of oxidizing or "wet-ashing" was devised. Like the similar method for total phosphorus, this depends upon the

assumption that vigorous oxidation destroys all organic matter and that the increased amount of inorganic arsenic found thereafter represents that which was previously combined in organic form and which was not previously revealed by the Gutzeit procedure. It must be kept in mind, however, that this assumption is not certain; for example, there may be resistant inorganic forms of arsenic—ionic or colloidal complexes—which are not thus brought within the scope of the analysis.

A measured sample of the sea water (about 750 ml.) was evaporated on a water bath to about 100 ml. After adding 10 ml. of 30% H_2O_2 and 5 ml. of conc. H_2SO_4, it was further concentrated to half the volume. It was then transferred to a Kjeldahl flask, and the dish washed twice with 2.5-ml. portions of H_2O_2. The flask was cautiously heated until gas evolution stopped, whereupon 2 ml. of conc. HNO_3 was added and the heating continued. At intervals of 10 or 15 minutes, two 5-ml. portions of H_2O_2 were added and the flask finally brought to vigorous boiling until the excess H_2O_2 was entirely decomposed.

The resulting arsenate was reduced with $NaHSO_3$ as previously described and arsenic determined by the modified Gutzeit method and the spectrophotometer.

TABLE II.—Vertical Distribution of Arsenic

Station 9. Longitude: 119° 26.5′ W. Latitude: 33° 0.5′ N.

Depth (*m.*)	*Arsenite*-As (μg. at./L)	*Total* As (μg. at./L)	As^{III}/*Total* As (%)
0	.16	.28	58
10	.20	.32	62
25	.25	.41	60
50	.15	.25	58
75	.11	.19	55
100	.13	.23	56
150	.19	.32	57
200	.16	.29	56
250	.16	.28	55
300	.12	.23	53
400	.20	.37	52
500	.19	.33	56
600	.13	.27	50

TABLE III.—Vertical Distribution of Arsenic

Station 11. Longitude: 118° 48.7′ W. Latitude: 33° 28′ N.

Depth (*m.*)	*Arsenite*-As (μg. at./L)	*Total* As (μg. at./L)	As^{III}/*Total* As (%)
0	.28	.49	57
10	.32	.52	61
25	.25	.43	60
50	.23	.39	59
75	.27	.45	59
100	.25	.43	60
150	.24	.44	56
200	.17	.33	54
250	.19	.36	54
300	.19	.33	56
400	.23	.44	52
500	.19	.35	54
600	.27	.53	50

TABLE IV.—Vertical Distribution of Arsenic

Station 16. Longitude: 118° 42′ W. Latitude: 32° 19′ N.

Depth (*m.*)	*Arsenite*-As (μg. at./L)	*Total* As (μg. at./L)	As^{III}/*Total* As (%)
0	.29	.48	62
10	.33	.59	57
25	.27	.48	60
50	.27	.45	58
75	.25	.43	59
100	.20	.37	55
150	.21	.40	56
200	.21	.41	54
250	.19	.37	52
300	.19	.37	52
400	.25	.48	52
500	.20	.41	50
600	.23	.48	48

TABLE V.—Vertical Distribution of Arsenic

Station 31. Longitude: 118° 06′ W. Latitude: 33° 20′ N.

Depth (*m.*)	*Arsenite*-As (μg. at./L)	*Total* As (μg. at./L)	As^{III}/*Total* As (%)
0	.20	.32	61
10	.25	.44	58
20	.17	.28	60
30	.27	.44	60
40	.24	.41	57
60	.23	.40	57
100	.16	.29	54
150	.19	.32	55
200	.12	.23	53
300	.13	.25	52
400	.19	.36	52
500	.17	.35	50

DISTRIBUTION OF ARSENIC IN SEA WATER

Arsenite-As and total arsenic were determined in water from different depths at four stations, as shown in Tables II, III, IV, and V. Values are given in microgram atoms of As per liter. The results for arsenite-As corroborate, in general, the earlier recorded analyses. There seems to be a slight tendency toward concentration in the upper levels, as well as a definitely higher ratio of arsenite to total arsenic.

Water from one station was used to determine the partition of arsenic among the four forms: arsenite, arsenate, particulate arsenic and dissolved organic arsenic. Results are shown in Table VI.

TABLE VI.—Distribution and Partition of Arsenic in a Water-column at Station 28. Longitude: 121° 23.5′ W. Latitude: 33° 5′ N.

Figures are in microgram atoms per liter

	1	2	2−1	3	4	4−2	3+4	5	
Depth (*m.*)	——*Inorganic*——			*Particulate*	*Filtrate*	*Dissolved Organic*	—*Total* As—		$\frac{As^{III}}{Total}$
	As^{III}	*Total*	As^{V}				*Sum*	*Direct*	(%)
0–25	.32	.39	.07	.08	.48	.09	.56	.53	60
50–100	.27	.31	.04	.03	.45	.15	.48	.48	56
150–250	.21	.27	.05	.05	.33	.07	.38	.40	53
300–500	.23	.25	.03	.01	.43	.07	.44	.43	53

In order to obtain sufficient water for the analysis, it was necessary to combine samples from adjacent depths and thus to divide the water column into four levels: 0–25 meters, 50–100 meters, 150–250 meters,

300–500 meters. Five analyses were made on each composite sample, shown in columns 1 to 5 in Table VI.

1. The simple method on the raw water (showing As^{III}).
2. The simple method after reduction (showing $As^{III} + As^{V}$).
3. After oxidation of the suspended matter in a filtered sample (showing particulate arsenic).
4. After oxidation of the filtrate from operation 3 (showing $As^{III} + As^{V}$ + dissolved organic arsenic).
5. After oxidation of the raw water (showing total of all forms of As).

Arsenate-As is obtained by subtracting 1 from 2; dissolved organic As by subtracting 2 from 4. All values are given in microgram atoms per liter.

It will be noted that about 55% of the total arsenic is present as arsenite, about 10% as arsenate, 10% as particulate arsenic, and 25% as dissolved organic arsenic.

It is well known that arsenate interferes with the determination of phosphate, increasing the apparent phosphate concentration proportionally. However, the extent of this interference is apparently negligible in most cases.

ARSENIC CONTENT OF SOME MARINE ANIMALS AND PLANTS

It is well known that marine organisms contain arsenic. The precise part, if any, played by it in their metabolism is uncertain, but it is possible that arsenic enters into the vital activities of the cell.

As a first step, the following marine specimens were analyzed for arsenic: *Octopus bimaculatus* (two-spotted octopus), *Mytilus edulis* (mussel), *Pisoster ochraceus* (ochre sea-star), *Macrocystis pyrifera* (brown kelp).

The samples were dried in an electric oven overnight at 110° C. A known weight was then transferred to a Kjeldahl flask, a 25-ml. mixture of HNO_3 and H_2SO_4 (1 : 1) was carefully added, and the flask slowly heated to foaming. Nitric acid was then added. The rate of addition depended upon the color of the solution, which was not allowed to turn brown. The digestion was continued with the addition of HNO_3 until the solution was water-clear. Heating was continued for an hour longer in order to destroy completely all the organic nitrogen compounds and to complete the removal of all traces of nitric acid. Wet ashing required a long time, especially in the case of the sea mussel and the digestive glands of the starfish; to hasten the process perchloric acid was added when most of the organic material was

oxidized. Care was taken to maintain a constant oxidizing condition and to avoid charring, in order to prevent the reduction of pentavalent arsenic, which is generally more easily volatilized.

Arsenate was reduced by heating at about 70° C. with 0.4 g. of $NaHSO_3$ for 60 minutes. The solution was then boiled to expel SO_2. An aliquot was withdrawn, arsine evolved, the color reaction carried out, and arsenic determined with the spectrophotometer. The results are shown in Table VII.

TABLE VII.—Arsenic Content of Marine Organisms

Specimen	*Arsenic (mg./kg.)*
Octopus bimaculatus (tentacles)	0.121 (wet weight)
Mytilus edulis	0.085 (wet weight)
Pisoster ochraceus	1.26 (dry weight)
Macrocystis pyrifera	17.3 (dry weight)

With such a high arsenic content (17.3 mg./kg. dry weight) *Macrocystis pyrifera* is concentrating arsenic as much as 1000 times the concentration of this element in the sea.

Sea anemones, which originally contained 6.6 mg. of As per kg. dry weight, were kept in two aquaria, to which increasing amounts of arsenite and arsenate, respectively, were added from time to time. Individual organisms were removed occasionally for analysis. The concentration of arsenic increased more rapidly in those exposed to arsenite. All animals died after exposure to concentrations up to 90 μg. of As^{III} per liter, at which point they contained 21.2 mg. of As per kg. dry weight. Animals exposed to concentrations of arsenate up to 160 μg. of As^{V} per liter were still alive and contained but 10 mg. of As per kg.

Anemones which had died from exposure to arsenite, as just described, were dried and found to contain 21.1 mg. of As per kg., which was distributed as follows: 91% in the protein fraction (88% being hydrolyzable), 1% in the lipid fraction, and 7% soluble inorganic arsenic. These results must be considered provisional, in view of the small amount of material dealt with.

SUMMARY

1. A modified and improved method for determination of arsenic is described.

2. The total arsenic present in sea water was found in amounts from 0.2 to 0.5 microgram atoms per liter. Of this, from 50 to 60% is in

the form of arsenite, and from 8 to 16% each of arsenate, dissolved organic arsenic, and arsenic in the suspended particulate matter. The relative proportion of arsenite was perhaps slightly greater in the upper levels.

3. The arsenic content of five marine organisms was determined (brown kelp, mussel, sea-star, two-spotted octopus, and sea anemone).

4. The sea anemone was found to tolerate larger concentrations of arsenate than of arsenite. Ninety per cent of the arsenic absorbed from high concentrations was found associated with protein.

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THE DETERMINATION OF PHOSPHATES IN SEA WATER

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The concentration of phosphates in sea water varies from 0.000 to about 2.00 microgram atoms (μg. atoms) phosphate-phosphorus per liter at 20° C. Occasionally a maximum of 3.00 μg. atoms may be found in some deep arms of the sea.

For the determination of the concentration of phosphate-phosphorus in sea water, the method of Denigès, as modified for the purpose, is recommended. The method itself is based on the principle that when a sulfuric acid solution of ammonium molybdate is added to a soluble phosphate solution a complex phosphomolybdic acid is formed. Upon treatment with a reducing agent, such as stannous chloride, the complex acid is reduced to a blue-colored substance believed to have the composition $H_3PO_4.(4MoO_3.MoO_2)_2.4H_2O$. The color developed is proportional to the concentration of the phosphate.

Arsenates give similar reactions with the ammonium molybdate and stannous chloride solutions. Arsenates, if present in sea water, occur in extremely small concentrations, probably less than 0.05 μg. atoms of arsenate-arsenic per liter of sea water. The procedure here given determines the sum of the arsenates and phosphates. For sea water containing more than 1 μg. atom of phosphate-phosphorus, the arsenates may be ignored, as the experimental error of the method will be greater than the actual amount of arsenic present.

The phosphorus and arsenic contained in organic compounds dissolved in the sea water, and in inorganic compounds other than phosphates and arsenates, have no influence upon the intensity of the blue color developed by the reagents.

Chemical Substances Required

1. Concentrated Sulfuric Acid (36 Normal)
2. Concentrated Hydrochloric Acid (12 Normal)
3. Ammonium Molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$
4. Stannous Chloride, $SnCl_2.2H_2O$
5. Metallic Tin, Mossy
6. Sodium Chloride, NaCl.
7. Anhydrous Potassium Dihydrogen Phosphate, KH_2PO_4
8. Chloroform, $CHCl_3$
9. Distilled Water

The above chemicals should all be pure substances and, with the exception of the potassium dihydrogen phosphate, free of phosphates and arsenates. Special emphasis must be given to the sulfuric acid, as this substance, used for most chemical purposes, often contains compounds of arsenic as impurities.

REGENTS

Distilled Water. If the distilled water shows a trace of phosphate, it should be redistilled after making alkaline with sodium or barium hydroxide.

Dilute Sulfuric Acid. 150 ml. 36 N sulfuric acid are slowly added to 150 ml. of distilled water contained in a beaker. After cooling, the solution is diluted to 300 ml.

Sulfuric Acid-Ammonium Molybdate solution. 10 g. of ammonium molybdate are dissolved in 100 ml. distilled water. This solution is added to 300 ml. of the 18 N sulfuric acid. The reagent must be kept in dark amber glass-stoppered bottles and protected from light to prevent photochemical reactions which will reduce the reagent. If this is done the solution should be stable for weeks.

Stannous Chloride Solutions

Solution I. 2.15 g. of the dihydrate of stannous chloride are dissolved in 20 ml. 12 N hydrochloric acid and diluted to 100 ml. with cooled distilled water which has been freshly boiled to remove the dissolved oxygen. A piece of mossy tin is placed in the solution to retard the oxidizing effects of the air. The solution is stored in amber glass-stoppered bottles and is very stable over a long period of time as long as metallic tin is present.

Solution II. 5 ml. of Solution I are diluted to 25 ml. with cooled distilled water which has been freshly boiled. A small piece of mossy tin is placed in the solution. On exposure to the air for a few hours, the solution will oxidize; thus, it is advisable to prepare a fresh supply of the solution each day. The oxidation may be materially retarded by placing a Mohr seal over the solution and siphoning off the amount necessary for immediate addition to the standards and samples. (The Mohr seal is a layer of paraffin oil.)

Sodium Chloride Solutions

Primary solution. 168 g. of sodium chloride are dissolved in distilled water and diluted to 5 liters. This solution contains 20‰ of chloride ions and may be used directly for the preparation of Standard Phos-

phate Solution III (as described below) when the chlorinity of the sea water under investigation is more than 18°/₀₀.

Diluted Solutions. For the preparation of the Standard Solutions III to be used when the chlorinity of the sea water under investigation is less than 18°/₀₀, diluted solutions of sodium chloride are prepared from the primary solutions. For this purpose 1 liter of a diluted solution containing k°/₀₀ of chloride may, with sufficient accuracy, be prepared by diluting 50 k ml. of the primary solution to 1000 ml. by means of distilled water.

Example: A sea water under investigation has a chlorinity of 15°/₀₀. Then 50 k is equal to 50 x 15, which is 750, and the desired sodium chloride solution is prepared by diluting 750 ml. of the primary sodium chloride solution to 1 liter by means of distilled water.

PREPARATION OF STANDARD PHOSPHATE SOLUTIONS

Emphasis must be given to the necessity for occasional check on all standard solutions. The statements given below are based upon the experience of many investigators. However, unknown factors may influence the stability of the solutions, and possible faulty technique of the investigator may cause alterations in the concentration of the standard solutions. Therefore, all standards must be subjected to rigorous control which may best be accomplished by preparation of duplicate standards from time to time.

Standard Solution I. 0.340 g. of pure anhydrous potassium dihydrogen phosphate, which has been previously dried to remove hygroscopic moisture, is dissolved in distilled water and transferred quantitatively to a 1 liter volumetric flask. The solution is diluted to volume, thoroughly mixed and 0.2 ml. chloroform added. 1 ml. of this solution contains 2.5 μg. atoms of phosphate-phosphorus. The addition of chloroform retards bacterial action. The solution is generally stable for about a year.

Standard Solution IIa. 10 ml. of Standard Solution I are pipetted into a 1 liter volumetric flask, diluted to volume by means of the primary solution of sodium chloride containing 20°/₀₀ of chloride ions, and the solution then thoroughly mixed. 1 ml. of this solution contains 0.025 μg. atom of phosphate-phosphorus. 0.2 ml. chloroform is added. The solution is generally stable for many weeks.

Standard Solution IIb. 40 ml. of Standard Solution I are diluted to 1 liter in a volumetric flask by means of the primary solution of sodium chloride containing 20°/₀₀ of chloride ions and thoroughly mixed.

1 ml. of this solution contains 0.10 μg. atom of phosphate-phosphorus. 0.2 ml. chloroform is added. The solution is generally stable for many weeks.

Standard Solutions III. These standard solutions are prepared by diluting a certain volume (from 0.10 ml. to 2.00 ml.) of Standard Solution IIa or IIb measured with a micro buret or Mohr pipet either to exactly 50 ml. or to exactly 100 ml. by means of a sodium chloride solution. The concentration of the sodium chloride solution used must be approximately in accordance with the chlorinity of the sea water that is to be investigated. If the chlorinity of the sea water is k °/₀₀, the chloride concentration of the sodium chloride solution must be between the limits, $k \pm 1$°/₀₀ Cl.

The number of standard solutions to be prepared depends upon the colorimetric method used and the phosphate-phosphorus concentration in the waters being investigated. The standard solutions given in Table I comprise those that are used when colorimetric estimations are made by means of Nessler tubes.

For certain waters with a relatively high concentration of phosphate 50 ml. Nessler tubes are utilized. For other waters with a lower concentration of phosphate 100 ml. Nessler tubes are to be preferred. The standard solutions may be prepared directly in the Nessler tubes if they are used. If Hehner cylinders or some form of a colorimeter are employed, selected standards are prepared according to the method of comparison.

The rapid formation of a yellow coloration and the gradual fading of the blue color in the saline solution necessitates the preparation of new Standard Solution III for each series of samples that are compared contemporarily with the standard solutions.

In the preparation of the Standard Solutions IIa, IIb and III, distilled water might be used instead of solutions of sodium chloride. Supposing that this is done, the color comparison of a sea water sample with a standard solution of the same concentration of phosphate shows that the color development and also the resulting color intensity are different for sea water and the standard solution. When sodium chloride solutions are used for preparation of the standard solutions these differences are in a considerable degree eliminated. Preferably the Standard Solutions IIa, IIb, and III are to be prepared by means of phosphate-free sea water of the same chlorinity as the sea water samples to be investigated. Should unforeseen conditions make it desirable to have the standard solutions prepared by means of distilled water this may be done, but the values found by a colorimetric determination of the concentration of phosphate in sea water are then to be multiplied by the factor, 1.15.

TABLE I.—Preparation of Standard Solutions III

Ml. of Standard Solutions IIa and IIb to be Diluted:		Concentration of the Prepared Standard Solutions when Diluted to:	
		50 ml.	*100 ml.*
IIa	IIb	IIa	IIb
		(*μg. atom of Phosphate-Phosphorus per liter of solution*)	
0.00	0.00	0.00	0.000
.10	—	.05	.025
.20	—	.10	.05
.40	—	.20	.10
.60	—	.30	.15
.80	—	.40	.20
1.20	—	.60	.30
1.60	—	.80	.40
2.00	—	1.00	.50
—	.60	1.20	.60
—	.70	1.40	.70
—	.80	1.60	.80
—	.90	1.80	.90
—	1.00	2.00	1.00
—	1.10	2.20	—
—	1.20	2.40	1.20
—	1.30	2.60	—
—	1.40	2.80	1.40
—	1.50	3.00	—
—	1.60	—	1.60
—	1.80	—	1.80
—	2.00	—	2.00

TESTING OF THE REAGENTS

A blank determination should always be made to insure the absence of phosphates and arsenates in the reagents and in the sodium chloride solution supposed to be free of these substances. This is accomplished by treating 50 ml. or 100 ml. of the primary sodium chloride solution with the reagents in the same manner as accorded the standards and the samples taken for analysis. If an appreciable color intensity is found in the blank determinations, new solutions are prepared successively in order that the contaminated reagent may be found and eliminated.

THE PROCEDURE FOR THE DETERMINATION OF THE CONCENTRATION OF PHOSPHATE-PHOSPHORUS IN SEA WATER

If the samples of sea water contain much plankton this should be removed by filtration or centrifugalization. However, it is only in extreme cases when such a procedure is necessary.

The samples for the phosphate determination are to be analyzed as soon as possible after they have been taken from the sea. Whether the determination is made by means of Nessler tubes or by any other method of comparison, it is recommended that 50 ml. or 100 ml. of the sea water sample be taken for the determination. The volumes of the standard solutions are determined by the volumes of the samples. The sea water samples and the standard solutions for the comparison are to be brought to the same temperature conditions so that the sea water sample and each of the standard solutions have temperatures within an interval of 2° C.

1 ml. of the sulfuric acid-ammonium molybdate reagent is added and mixed with each of the standard solutions and sea water samples. About 0.20 ml. of Stannous Chloride Solution II is likewise added and thoroughly mixed with each sample and standard solution. Maximum color intensity develops in about seven minutes and comparisons are then made with the standards. About twelve samples can be conveniently handled at a time. It is recommended that samples should not be stored for more than a few hours before the analyses are made and that they should not be exposed to direct sunlight while awaiting temperature equilibrium with the standard solutions.

Should conditions necessitate comparison with standards made from distilled water, then the concentration values for phosphate-phosphorus shown in Table I must be multiplied by the factor, 1.15.

Nessler tubes used for phosphate determinations soon become coated with a blue reduction compound of molybdenum that hinders the matching of the colors being produced in the tubes. Thus, it is important to clean the tubes occasionally with aqua regia. If other forms of apparatus are used a similar cleaning is essential.

Caution must be observed that glassware is not used alternately for phosphate and for silicate determinations without thoroughly cleaning with aqua regia between each type of determination.

Accuracy of Results. The accuracy of the determination is about 5 to 10 per cent. Because of the very small concentrations of phosphate in sea water, correction is not necessary for the slight deviation in volume of sea water due to the deviation in temperature from 20° C. This statement also applies to the standard solutions.

APPARATUS REQUIRED

In accordance with the above description, the following solutions and apparatus are recommended for use aboard ship. It is assumed that ample provision will be made for taking duplicate solutions and apparatus in case of accident or breakage. Duplicate materials and solutions should always be packed in separate containers.

1. Apparatus for sampling the sea water.
2. Amber glass-stoppered bottles 250–500 ml. capacity with sulfuric acid-ammonium molybdate solution.
3. Amber glass-stoppered bottles 50–100 ml. capacity with Stannous Chloride Solution I.
4. Amber glass-stoppered bottles 50–100 ml. capacity with Stannous Chloride Solution II.
5. Bottles or demijohns of sufficient capacity with primary solution sodium chloride.
6. Bottles or demijohns of sufficient capacity with distilled water.
7. Amber glass-stoppered bottles of capacity 100–250 ml. with Standard Solution I.
8. Amber glass-stoppered bottles of capacity 100–250 ml. with
   (a) Standard Solution IIa, and
   (b) Standard Solution IIb.
9. Apparatus for preparation of standard solutions:
   (a) 10 ml. pipet, calibrated;
   (b) 1000 ml. volumetric flask, calibrated;
   (c) Pipet of capacity 0.2 ml.;
   (d) 5 ml. microburet, graduated to 0.05 ml.;
   (e) Buret stand;
   (f) A suitable number of Erlenmeyer flasks, 125 ml. capacity, for preparation of standard solutions for comparison with sea water according to the method used for the color comparison; the standard solutions may be prepared directly in the Nessler tubes, thus making the Erlenmeyer flasks unnecessary.
10. Filtering or centrifuging apparatus for removing plankton from the sea water if necessary.
11. Apparatus for applying the reagents to the standard and sea water samples:
    (a) Measuring flasks or cylinders of capacity 100 ml., 50 ml., and 25 ml. If Nessler tubes are used and if these are marked to the volumes 100 ml. and 50 ml., respectively, the measuring flasks may be unnecessary.

(b) Pipet marked to deliver 1 ml. of the sulfuric acid-ammonium molybdate reagent.
(c) Pipet marked to deliver 0.2 ml. of the solution of Stannous Chloride Solution II.

12. Apparatus for colorimetric measurements:
(a) Nessler tubes with *graduation marks at the same height* (diameter of 20 mm. and 16 mm. for tubes containing 100 ml. and 50 ml., respectively) may be convenient, or
(b) Hehner cylinders, or
(c) Colorimeter, visual or photoelectric, or
(d) Photometer.
13. Thermometer graduated to 1° C.
14. Bottles with distilled water for cleaning the measuring apparatus when necessary.

NOTES ON THE DETERMINATION

1. Organic phosphorus and the lower valence compounds of phosphorus are not determined by this method unless special treatment is given the sample. Arsenates, if present, yield a blue reduction color by this method.
2. With low concentration of phosphate there is a proportionately greater reduction color than would be expected.
3. If the hydrogen-ion concentration in the molybdate reagent is insufficient, the stannous chloride reduces the reagent itself as well as the complex phosphomolybdic acid. If the hydrogen-ion concentration is too great the sensitivity of the reagent is reduced materially.
4. By dissolving the solid stannous chloride dihydrate in concentrated hydrochloric acid and then diluting, hydrolysis is prevented.
5. Upon prolonged standing the concentration of the dilute standard phosphate solutions is often materially reduced because of bacterial action. This may be prevented by the introduction of a small amount of chloroform.
6. The samples should be analyzed for phosphate as soon as possible. If this is not done, errors may result. First, the phosphate concentration may be appreciably reduced through phytoplanktonic action, and second, the phosphate concentration may increase through bacterial or enzymatic action on the organic phosphorus which exists in solution, or suspension.
7. Temperature affects the equilibrium established in the reaction. The standards and samples should thus be near the same temperature during color development and comparison. For example, if the phosphate is determined in two solutions of the same concentra-

tion but the temperature of one in 15° C. and the other 30° C., the intensity of the reduction color in the warmer is noticeably greater.

8. Three drops of stannous chloride solution are often recommended in this determination, but as mentioned previously a yellow color is formed in sea water when this is done. Reducing the quantity to one drop still leaves a twelve-fold excess above the theoretical amount probably required and at the same time reduces the intensity of the yellow coloration so that it does not interfere materially. The intensity of the blue color is reduced about ten per cent at the same time.

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THE DETERMINATION OF NITRITES IN SEA WATER

By

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The concentrations of nitrite-nitrogen in sea water varies from 0.000 to 2.00 microgram atoms (μg. atoms) per liter of sea water at 20° C. In the open ocean nitrites are seldom found in depths below 100 meters, and even at these depths the water may be completely devoid of nitrites. When occurring in waters near the surface, the concentration is generally less than 0.10 μg. atom of nitrite-nitrogen per liter. The higher values are obtained at times in the waters on the continental shelf and in sounds, straits, fjords and estuaries.

The method recommended for the determination of nitrites, shown by the chemical equation

$$HSO_3.C_6H_4.NH_2 + HNO_2 + C_{10}H_7.NH_2 \rightarrow HSO_3.C_6H_4.N : N.NH.C_{10}H_7 + 2H_2O,$$

was originally developed by Peter Griess and later modified by Ilosvay. This method depends upon the diazotization of the amines in acid solution by the nitrite in the sea water. The product of this reaction is a rose-colored dye whose color intensity is proportional to the quantity of nitrite present.

Chemical Substances Required:

1. Sulphanilic Acid, $HSO_3.C_6H_4.NH_2$
2. Alpha-naphthylamine, $C_{10}H_7.NH_2$
3. Sodium Nitrite, $NaNO_2$
4. Glacial Acetic Acid, CH_3COOH
5. Mercuric Chloride, $HgCl_2$
6. Distilled Water
7. Sodium Chloride, NaCl
8. Chloroform, $CHCl_3$

The above chemicals should all be pure substances and, with the exception of sodium nitrite, must be free of nitrites. The first five listed should be stored in bottles of amber glass with glass stoppers, while the other materials should be kept in glass-stoppered bottles made of resistant glass.

REAGENTS

Distilled Water. Occasionally it is difficult to obtain distilled water free of nitrites. Should this be the case, suitable water may be secured by redistilling after making alkaline with sodium or barium hydroxide.

Sulphanilic Acid. One gram of the substance is dissolved by heating in a mixture of 15 ml. glacial acetic acid and 15 ml. of distilled water. More water is gradually introduced to the warm solution with constant stirring until 270 ml. of water have been introduced and the material has been dissolved. The solution should be stored in a glass-stoppered bottle of amber glass.

Alpha-naphthylamine. 0.2 g. of the substance is boiled with 40 ml. of distilled water. The colorless solution is decanted (while hot) from the dark-colored precipitate and treated with 15 ml. glacial acetic acid. This solution is diluted with 285 ml. distilled water. The solution should be stored in an amber, glass-stoppered bottle.

Sodium Chloride. 160 g. of sodium chloride are dissolved in 5 liters of distilled water and stored in suitable containers.

In place of sodium chloride solution, a nitrite-free sea water may be used. This water may often be obtained from the open ocean at depths below 200 meters. To prevent bacterial action, 5 ml. of a saturated solution of mercuric chloride are added per liter of sea water. This nitrite-free sea water is stored in the dark in demijohns or other suitable containers.

If nitrite-free sea water can not be obtained directly, it may be prepared by taking 4 liters of filtered sea water acidified with 0.5 ml. of glacial acetic acid and boiled for 45 minutes. The boiling operation is repeated on several successive days until the water is nitrite free. Evaporation losses are replaced by nitrite-free distilled water. To prevent bacterial action, 20 ml. of a saturated solution of mercuric chloride are added and the solution stored in a suitable container.

The rate of color development and not the final color intensity is affected by the presence of salts in solution. The development of the rose color with the reagents is much more rapid in sea water than in distilled water. Maximum intensity in the salt solutions and sodium chloride solutions is reached within 30 minutes, while with distilled water as much as two or three hours may be required. Increase in temperature likewise promotes the speed with which the reactions take place.

PREPARATION OF STANDARD NITRITE SOLUTIONS

In the preparation of standard solutions, sodium nitrite is used. However, silver nitrite may be used, if a relevant technique is applied. The former compound is recommended in the preparation of the following solutions because of its greater convenience.

Emphasis must be given to the necessity for occasional check of all standard solutions.

The statements given below are based upon the experience of many investigators. However, unknown factors may influence the stability of the solutions, and possible faulty technique of the investigators may cause alterations in the concentration of the standard solutions. Therefore all standard solutions must be subjected to rigorous control which may best be accomplished by preparation of duplicate standards from time to time.

Standard Solution I. Sodium nitrite is recommended for the preparation of standard nitrite solutions. A few grams of pure sodium nitrite are dried for about four hours in an oven at 110° C. and cooled in a desiccator. Other adequate drying methods for the removal of hygroscopic water may also be used. 0.690 g. of the dried sodium nitrite is carefully weighed, transferred to a suitable container and dissolved in nitrite-free distilled water. The solution is transferred quantitatively to a liter volumetric flask, diluted to volume and thoroughly mixed. 0.2 ml. of chloroform or carbon disulfide is added as a preservative which insures a stable solution over many months. This solution is stored in tightly stoppered bottles and kept in the dark. Preparation of duplicate solutions is recommended. 1 ml. = 10 μg. atoms nitrite-nitrogen.

Standard Solution II. 5 ml. of the Standard Solution I are pipetted into a 500 ml. volumetric flask, diluted to volume with nitrite-free distilled water and thoroughly mixed. 1 ml. of this solution contains 0.10 μg. atom nitrite-nitrogen. This diluted standard solution is usually stable for several days. On longer standing the concentration may be lowered due to chemical or bacterial action. In some cases experience has shown that this solution may be stable for several months; however, good practice demands careful control.

Standard Solutions III. These standard solutions are prepared by diluting a certain amount (from 0.10 ml. to 1.00 ml.) of Standard Solution II to exactly 100 ml. with sodium chloride solution of nitrite-free sea water.

The number of standard solutions to be prepared depends upon the colorimetric method used. The standard solutions, given in Table I,

comprise those that are used when the colorimetric comparisons are made by means of Nessler tubes. If the colorimetric estimation is made with Hehner cylinders or with some form of colorimeter, then only one or two standard solutions are necessary.

The standard samples may be prepared and stored directly in the relevant containers for the colorimetric measurement (Nessler tubes, Hehner cylinders, etc.).

TABLE I. PREPARATION OF STANDARD SOLUTIONS III

Milliliters of Standard Solution II diluted to 100 ml.	Concentration of Standard Solutions III ($\mu g.$ *atoms* NO_2-*N per liter of solution*)
0.00	0.00
.10	.10
.20	.20
.40	.40
.60	.60
.80	.80
1.00	1.00

Instead of sodium chloride solution or nitrite-free sea water, nitrite-free distilled water may be used for the preparation of the standard solutions for comparison with sea water from Standard Solution II, but sufficient time must be allowed for full color development.

TESTING THE REAGENTS

When the standard solutions for comparison with the sea water are prepared, a blank determination should always be made to insure the absence of nitrites in the solutions used. This is accomplished by treating 100 ml. of the sodium chloride solution or nitrite-free sea water or distilled water with the reagents in the same manner as accorded to the standards and samples taken for analysis.

THE PROCEDURE FOR THE DETERMINATION OF THE CONCENTRATION OF NITRITE-NITROGEN IN SEA WATER

The samples for the nitrite determination are treated with the reagents as soon as possible after they have been taken from the sea.

Whether the determination is made by means of Nessler tubes or by any other method, it is recommended that 100 ml. samples of sea water be taken for the determination.

Equal volumes of sulphanilic acid and alpha-naphthylamine acetate are thoroughly mixed. 4 ml. of the mixture are added to each standard

solution and sea water sample. The treatment of the standard solutions and the sea water samples must be the same. However, in cases where a number of samples are being collected over a period of days, the same standard solution for comparison may be used throughout a twenty-four hour period. Before the color comparisons are made, the temperatures of the standards and of the samples of sea water should not differ by more than 2° C. The comparisons of the samples with the standards may be made 30 minutes after temperature equilibrium has been obtained. If the color of one of the 100 ml. samples of sea water matches, for example, with that of the standard containing 0.60 ml. of Standard Solution II which has been diluted to 100 ml., then the sea water contains 0.60 μg. atom nitrite-nitrogen per liter.

Should it be impossible to make color comparisons shortly after the sea water samples have been secured, the standards and the samples should be stored in the dark until conditions are more auspicious. The color is constant for four or five days. In any event, the mixture of reagents must be added as soon as the samples have been collected.

If difficulty is experienced in making color comparisons by means of Nessler tubes because of marked color intensity, then a smaller sample must be taken. A 50 ml. or even a 25 ml. sample of sea water is diluted with sodium chloride solution or nitrite-free sea water to 100 ml. in a Nessler tube and treated with 4 ml. of the mixed reagents. The nitrite-nitrogen concentration will be twice as great as indicated in Table I if a 50 ml. sample of sea water is used, and four times as great if a 25 ml. sample is taken.

Accuracy of Results. The accuracy of the determination is about 5 to 10 per cent. Because of the very small concentrations of the nitrites in sea water, no correction is necessary for the slight deviation in volume of sea water due to the deviation in temperature from 20° C. This statement also applies for the standard solutions used.

APPARATUS REQUIRED

In accordance with the above description, the following solutions and apparatus are recommended for use on board ship. It is assumed that ample provision will be made for taking duplicate solutions and apparatus in case of accident or breakage. Duplicates of materials and solutions should always be packed in separate containers.

1. Apparatus for sampling the sea water.
2. Amber glass-stoppered bottles 100–250 ml. capacity with sulphanilic acid solutions.

3. Amber glass-stoppered bottles 100–250 ml. capacity with alpha-naphthylamine acetate solutions.
4. Amber glass-stoppered bottles 100–250 ml. capacity with Standard Solution I.
5. Bottles or demijohns of sufficient capacity for nitrite-free sea water, sodium chloride solution or distilled water.
6. Apparatus for preparation of standard solutions:
   (a) 5 ml. pipet;
   (b) 500 ml. glass-stoppered volumetric flask;
   (c) Glass-stoppered bottles of 500 ml. capacity to contain the Standard Solution II;
   (d) 5 ml. microburet, graduated to 0.05 ml., with buret stand;
   (e) A suitable number of Erlenmeyer flasks, 125 ml. capacity, for preparation of the standard solutions for comparison with sea water according to the method used for the color comparison. If Nessler tubes are used for the color comparison, the standard solutions may be prepared directly in the Nessler tubes, thus making the Erlenmeyer flasks unnecessary.
7. Apparatus for mixing the solutions of sulphanilic acid and alpha-naphthylamine acetate solutions and applying the mixture to the standards and samples:
   (a) 100 ml. graduated cylinder;
   (b) 100 ml. bottle with a Mohr pipet, graduated to deliver 4 ml.
8. Apparatus for colorimetric measurements:
   (a) 24 100 ml. Nessler tubes with graduation marks at the same height (diameter of 20 mm. may be convenient), or
   (b) Hehner cylinders, or
   (c) Colorimeter, or
   (d) Photometer.
9. Thermometer graduated to 1° C.
10. Bottles with distilled water for cleaning the measuring apparatus necessary.

OTHER METHODS

The use of the dimethyl derivative of alpha-naphthylamine has been proposed, but it has no particular advantage. The diethyl derivative has been found to give a more stable color. The indol method, used many years ago, while giving fair results, is rather unsatisfactory because of the gradual decrease in color intensity after 45 minutes.

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THE DETERMINATION OF SILICATE IN SEA WATER

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The normal range of silicate in sea water is from 0.0 to about 200 μg. atoms Si per liter at 20° C. It has not been fully demonstrated whether the silicate determined by the method described below is in the colloidal or ionic form or both.

A colorimetric method for the determination of silicate in mineral water was modified and made practical by Dienert and Wandenbulcke. Atkins was the first to apply the method to oceanographic investigations.

The slightly modified method of Dienert and Wandenbulcke is the most accurate and convenient for the estimation of such concentrations of silicate. By this method silicate with the proper hydrogen-ion concentration is converted by molybdate to a yellow-colored compound which is probably the heteropoly acid, $H_8Si(Mo_2O_7)_2$. Ferric and phosphate ions in sufficient concentration are known to interfere with the determination of silicate, but the concentrations of these substances in sea water is such that their effect is negligible.

Chemical Substances Required:

1. Concentrated Sulfuric Acid (36 Normal)
2. Ammonium Molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$
3. Potassium Chromate, K_2CrO_4
4. Borax, $Na_2B_4O_7.10H_2O$
5. Picric Acid, $C_6H_2.(NO_2)_3.(OH)$
6. Distilled Water

The sulfuric acid and ammonium molybdate reagents should be silicate-free. The distilled water used in the preparation of these reagents should also be silicate-free. Since silicate is extracted from glass by the distilled water, silicate-free distilled water should be stored only in nonglass containers.

Potassium chromate should be purified by recrystallization from water solution.

Picric acid often contains water and other impurities. To purify it, 40 g. are dissolved in hot benzene, separated from the water, and fil-

tered to remove insoluble material. The benzene is evaporated under reduced pressure until water globules appear. The benzene solution is separated by decantation, and evaporation is continued until the picric acid is dry. The dry picric acid is stored in sealed vials until ready for use.

REAGENTS

Dilute Sulfuric Acid. 5 ml. of concentrated sulfuric acid are diluted to 30 ml. with silicate-free distilled water.

Ammonium Molybdate. 10 g. of $(NH_4)_6Mo_7O_{24}.4H_2O$ are dissolved in 100 ml. of silicate-free distilled water.

Borax Solution. 10 g. of $Na_2B_4O_7.10H_2O$ are dissolved to form a liter of solution.

STANDARD SOLUTIONS

Solutions of sodium silicate, analyzed gravimetrically for their silicate content, have been used for the preparation of standards by dilution. This is a laborious process and the standards are stable for only limited periods. More permanent standards are easily prepared from either potassium chromate or picric acid solutions. Several investigators have determined the silicon equivalency of these solutions for this method of estimation. Experience has shown that a more readily reproducible standard solution may be prepared from a buffered solution of potassium chromate than from picric acid solution.

Potassium Chromate Solution I. 0.945 g. of K_2CrO_4 which have been dried at 105° C. are dissolved in distilled water and diluted to 1 liter. 1 ml. of this solution is equivalent to 2.5 μg. atoms Si.

Potassium Chromate Solutions II. These are prepared by diluting appropriate volumes of Standard Solution I to 50 ml. with 25 ml. of one per cent borax solution and distilled water. The concentration and number of standards II to be prepared are dependent upon the manner of comparison to be used and the concentration of silicate in the unknowns under investigation. In Table I are shown the dilutions when using Nessler tubes. For high concentrations of silicate, the 50 ml. tubes are recommended, while 100 ml. tubes are to be preferred for low concentrations.

Picric Acid Standard Solution I (Alternate Standard). 76.7 mg. of the pure, dried picric acid are dissolved in distilled water and diluted to a liter. 1 ml. of this solution is equivalent to 2.5 μg. atoms Si, which is the same equivalency as the potassium chromate Standard Solution I; consequently it may be diluted as indicated in Table I.

TABLE I. PREPARATION OF STANDARD POTASSIUM CHROMATE SOLUTIONS II

Milliliters of Standard Solution I Diluted to:	Concentration of Standard Solutions II when Diluted to:	
	50 ml.	*100 ml.*
50 or 100 ml.	*(μg. atom Si per liter of solution)*	
0.20	10	5
.40	20	10
.60	30	15
.80	40	20
1.00	50	25
1.20	60	30
1.40	70	35
1.60	80	40
1.80	90	45
2.00	100	50
2.40	120	60
2.80	140	70
3.20	160	80
3.60	180	90
4.00	200	100

It seems to be generally agreed that in a sea water medium a given amount of silicate develops less yellow color with the reagents than it does in a distilled water medium. No such agreement exists concerning the magnitude of this "salt effect" or how it varies, if at all, with changing chlorinity. Consequently, the above standards have been left uncorrected for this factor.

TESTING THE REAGENTS

The reagents should be tested occasionally for silicate impurities. The amount of reagents, as specified in the procedure, should be added to silicate-free distilled water. If at any time the reagents become contaminated with large amounts of silicate, new reagents should be prepared. If only small amounts are present, the appropriate correction can be deducted from each observed value when comparing the unknowns with the "permanent" standards.

THE PROCEDURE FOR THE DETERMINATION

The samples of water should be taken from the sampling bottles immediately after bringing them aboard ship. They should be taken directly in the Nessler tubes for analysis. When comparisons are to be made in a colorimeter or photometer, samples are drawn from the water bottle into a graduated cylinder, transferred to a 125 ml. Erlenmeyer flask. Plankton or sediment need not be removed from the sample when present only in small amounts. 0.5 ml. of ammonium molybdate reagent and 0.25 ml. of 6N sulfuric acid are added for each

50 ml. of sample. Comparison should be made with the standards not sooner than 5 to 10 minutes or longer than 1 hour after development of color.

NOTES ON THE DETERMINATION

1. The borax solution acts as a buffer in the regulation of the pH of the solution. This is necessary to insure a constant equilibrium between the chromate and dichromate ions. The alkalinity of the buffer solution favors the formation of the yellow-colored ion.

$$2\ CrO_4^{=} + 2\ H^+ \rightleftarrows Cr_2O_7^{=} + H_2O\,.$$

2. The Chromate Standard Solutions II do not deteriorate on standing, but as a precaution new Solutions II should be prepared every six months. Solution I is stable indefinitely.

3. Picric Acid Standards are not as stable as the Chromate Standards. The ordinary C.P. picric acid contains varying quantities of water, and thus the compound should never be used without first removing the water and recrystallizing from benzene.

4. Picric Acid Standards should never be prepared by dilution with sea water as the dissolved salts have a decided "salt effect" upon the tautomeric equilibrium existing in the picric acid solutions.

5. If the samples are not analyzed immediately, they should be treated with the required amount of sulfuric acid in the Nessler tubes and then with the ammonium molybdate at a later time when the comparisons are to be made. In this manner samples may be preserved for about a day. It should be emphasized that comparisons with the standards should be made as soon as possible.

6. Under no circumstances should samples be stored in glass bottles for future analysis. Sea water acts rapidly on glass; therefore, samples that have been stored in glass containers for any length of time give high results and are valueless.

7. Samples containing large quantities of plankton or of sediment when stored in nonglass containers for any period of time give high results which are valueless.

8. Both the meta- and orthosilicates are analogous in their behavior toward the molybdate reagent, as might be expected, since in water solution orthosilicate has been shown to be converted to metasilicate.

9. A maximum error of 5 per cent occurs when Nessler tubes are employed, and this may be reduced somewhat by the employment of a colorimeter or photometer.

10. Nessler tubes which have been used for the phosphate determination should not be used for the determination of silicate, as color difficulties are often experienced if this is done.

11. A greenish tinge is sometimes obtained with water having more than 70 μg. atoms Si per liter, especially when Nessler tubes are employed. This interference may be eliminated by the use of the photometer or by proper dilution of a smaller water sample.

12. Should it be deemed desirable to dilute samples high in silicates with distilled water, an analysis should first be made on the latter to ascertain its silicate content.

13. With waters of low silicon values, 100 ml. samples should be utilized. A sensitivity is obtained with Nessler tubes equivalent to 2 parts of Si in 100,000,000 parts of water.

14. Temperature has little effect upon the color intensity of the yellow heteropoly acid. However, the color development is slower at low termperatures, so that a longer time should be given. With a temperature of 5° C., half an hour is needed.

15. An excess of sulfuric acid causes a diminution in the color intensity, but no effect is noted with slight excesses of the molybdate reagent. The yellow color of the heteropoly acid reaches its maximum intensity within 5 minutes after the addition of the reagents and remains constant for nearly three hours. However, the samples should be compared with standards as soon as possible to avoid any increase in silicate concentration by the action of the sea water on the glass containers.

16. While the presence of compounds of iron and phosphorus may interfere with the determination, their occurrence in sea water is of such a concentration that any error from this source is negligible.

17. The silicon should be reported as microgram atoms of silicon per liter of water.

APPARATUS AND SOLUTIONS REQUIRED

In accordance with the above description, the following solutions and apparatus are recommended for use aboard ship. It is assumed that ample provision will be made for taking duplicate solutions and apparatus in case of accident or breakage. Duplicate materials and solutions should always be packed in separate containers.

1. Apparatus for sampling sea water (sampling apparatus).
2. Amber glass-stoppered bottle, 100 ml. capacity, for 6N sulfuric acid.
3. Amber glass-stoppered bottle, 100 ml. capacity, for ammonium molybdate reagent.
4. Bottles of sufficient capacity for distilled water.
5. Metal containers of sufficient capacity for distilled water.

6. Glass-stoppered bottles of 500-ml. capacity for Standard Solution I.
7. 500 ml. glass-stoppered bottles for borax solution.
8. Apparatus for preparation of standard solutions and reagents:
   (a) Balance accurate to 0.1 mg.;
   (b) 100 ml. graduated cylinder;
   (c) 25 ml. graduated cylinder;
   (d) 1000 ml. volumetric flask, glass-stoppered;
   (e) 5 ml. pipet, graduated to 0.1 ml.
9. Apparatus for measuring samples and reagents:
   (a) If Nessler tubes are not used, an ample number of 125 ml. Erlenmeyer flasks made of Pyrex glass (or its equivalent) should be provided;
   (b) 1 ml. pipet graduated to 0.01 ml.;
   (c) 1 ml. pipet graduated to 0.1 ml.
10. 250 ml. beakers of Pyrex glass or equivalent, and 1000 ml. beakers of Pyrex glass or equivalent.
11. Apparatus for colorimetric measurement:
   (a) Nessler tubes with graduation marks at same height (100 ml. tubes of 20 mm., and 50 ml. tubes of 16 mm. diameter, are convenient) or
   (b) Hehner cylinders, or
   (c) Colorimeter, or
   (d) Photometer.

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NOTE CONCERNING HUMAN RESPIRATORY IRRITATION ASSOCIATED WITH HIGH CONCENTRATIONS OF PLANKTON AND MASS MORTALITY OF MARINE ORGANISMS[1]

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There is increasing evidence that high concentrations of plankton are sometimes associated with mass mortality among marine animals (Taylor, 1917, see ref's pp. 14–16; Marchand, 1928; Brongersma-Sanders, 1947; Gunter, et al., 1947).

Human respiratory irritations, also concurrent with mass mortality of fish, have been recorded by Taylor (1917), Lund (1934–35), and Gunter, et al. (1947). The respiratory irritant, commonly termed a gas, is said to produce hard coughing and a burning sensation in the nose, throat and lungs. This irritation is reported to occur in persons near the shore during onshore winds, as well as on the open sea.

This paper gives support to the work of Somner, et al. (1937), which indicates that certain dinoflagellates produce irritating or poisonous effects when present in high concentrations. It is the purpose of this paper to list qualitative subjective tests which show that the above-mentioned respiratory irritation is associated with the presence in the inhaled air of minute drops originating in sea water discolored by high concentrations of dinoflagellates.

The presence of sea water nuclei in oceanic air under ordinary conditions is well known (Owens, 1926; Jacobs, 1937, 1939; Cunningham, 1942; and Dessens, 1947). These nuclei are sometimes crystalline, sometimes liquid, depending upon the relative humidity of the ambient air. This phase change usually occurs somewhere between 60 and 75% relative humidity (Owens, 1926; Wright, 1939; and Dessens, 1947). The nuclei vary in radius from about 0.3 to 30μ. These aerosols from the sea are probably formed by bursting bubbles from breaking waves in a manner similar to that shown to occur in effervescing H_2O (Stuhlman, 1932). Zobell (1940) has found that marine bacteria exist in oceanic air and he suggests that they are carried into the air by sea water nuclei produced by spray. Therefore it is reasonable to suppose

[1] Contribution No. 389 of the Woods Hole Oceanographic Institution.

that other organisms or products of the sea are also carried up from the sea surface film by these spray drops.

At the request of the United States Fish and Wildlife Service, the author visited Venice, Florida in July 1947 when great numbers of fish were dying along the local shores of the Gulf of Mexico. Light offshore winds prevailed at this time and reports of human respiratory irritations[2] had recently ceased. Since the presence of this irritation was reported as associated with "red water," dying fish and onshore winds, it was reasonable to test some of the discolored water. During July and August 1947 the following simple tests and experiences were recorded.

Samples of sea water of a deep reddish shade were taken on July 24, 1947, about 5 miles offshore[3] at Lat. 27° 14′ 15″ N., Long. 82° 39′ 10″ W. These samples were unconcentrated sea water collected by dip-bucket. They were found to contain from 15 to 56 million dinoflagellates per liter. (The greatest number, *i. e.* 56 x 10^6 dinoflagellates per liter, is about four times the maximum reported by Allen [1941] in a twenty years' statistical study of marine dinoflagellates of southern California). These dinoflagellates were about 25 microns in diameter and were identified as *Gymnodinium* sp. by F. G. Walton Smith and Paul S. Galtsoff (personal communications). When sea water containing 56 x 10^6 dinoflagellates per liter was sprayed into the nose and throat with a hand atomizer, coughing and a burning sensation in the nose and throat resulted. This effect is apparently similar to that experienced along local beaches during onshore winds. This test was repeated many times with the same results. Relatively clear sea water from another local area produced no similar irritation.

During July 24 and 25, 1947, the author and two companions spent about five hours at sea, near and immediately over large patches of "red water." For long periods of time we worked over tubs of this water, over nets slimy with concentrated plankton and decks awash with spilled "red water." Winds during this time did not exceed 3 m/sec and there were no white caps on the sea surface. We noted no respiratory trouble of any kind throughout this period. However, on the afternoon of the 24th a thunder squall with heavy rain and a force 5 wind (from the east) passed over. During this squall, of about 30 minutes duration, the sea surface became streaked with foam, which was presumably caused by breaking waves and the impact of heavy rain on the surface water. During the latter part of the passage of

[2] Detailed information concerning the objective symptoms of this respiratory irritation may be secured from Dr. T. S. Thompson, M.D., Box 224, Venice, Florida.

[3] "Red water" from this area was found to contain unusually high concentrations of phosphorus (see Ketchum and Keen, 1948).

this squall we experienced coughing and a burning sensation in the nose and throat. After the wind subsided and the white caps and foam streaks disappeared, the respiratory irritation also dispapeared. Thus the presence of an irritant in the free air over the "red water" seemed to be correlated with increased wind and with the presence of breaking waves and foam. Sampling of aerosols at this time was prevented by the rain.

About 20 cm.^{3} of the sea water containing 56 x 10^6 dinoflagellates per liter was passed through a Jena fritted glass bacteria filter which had 1 to 1.5 micron openings. This filtrate produced the same irritation as did the unfiltered water when it was sprayed into the nose and throat with an atomizer. No particulate matter was seen in this filtrate under the microscope, using a magnification of 500×.

Samples of the "red water" were placed in shallow aluminum pans and heated. At temperatures varying from 80° to 90° C, clouds of fine bubbles formed in this water. These bubbles rose to the surface and burst, causing the hissing sound of effervescence. Coincident with the formation of these clouds of small bursting bubbles, the vapor rising from the surface produced involuntary coughing and a burning sensation in the nose and throat. When the heat source was removed, the bubbling quickly ceased and the irritating effects of the vapor also ceased. Upon reapplication of the heat and the reformation of the clouds of fine bubbles, the irritating effect of the vapor was again present. When the relatively clear sea water was heated in this manner, no irritating effects could be detected upon inhaling the vapors.

Small (1 x 10 mm.) glass slides, covered with a hydrophobic film, were exposed for 10 seconds at a height of 2 cm. above various vessels, some containing clear sea water and others containing "red water," under different conditions of temperature and effervescence. Table I

TABLE I.

	"Red Water"				*Relatively Clear Sea Water*			
	Bubbling		*No Bubbles*		*Bubbling*		*No Bubbles*	
T°C	*26°*	*85°–95°*	*26°*	*85°–95°*	*25°*	*85°–95°*	*25°*	*85°–95°*
Drop diameters (microns)	15–80 (estimate)	15–80 (estimate)	no drops	no drops	15–80	15–80	no drops	no drops
Respitory Irritation	Yes	Yes	No	No	No	No	No	No

shows the conditions under which drops were or were not deposited on these glass slides, the size range of these drops,[4] and the occurrence of

[4] The isopiestic technique used to cause these small drops to assume their original concentration and size under the microscope will be described in a later publication.

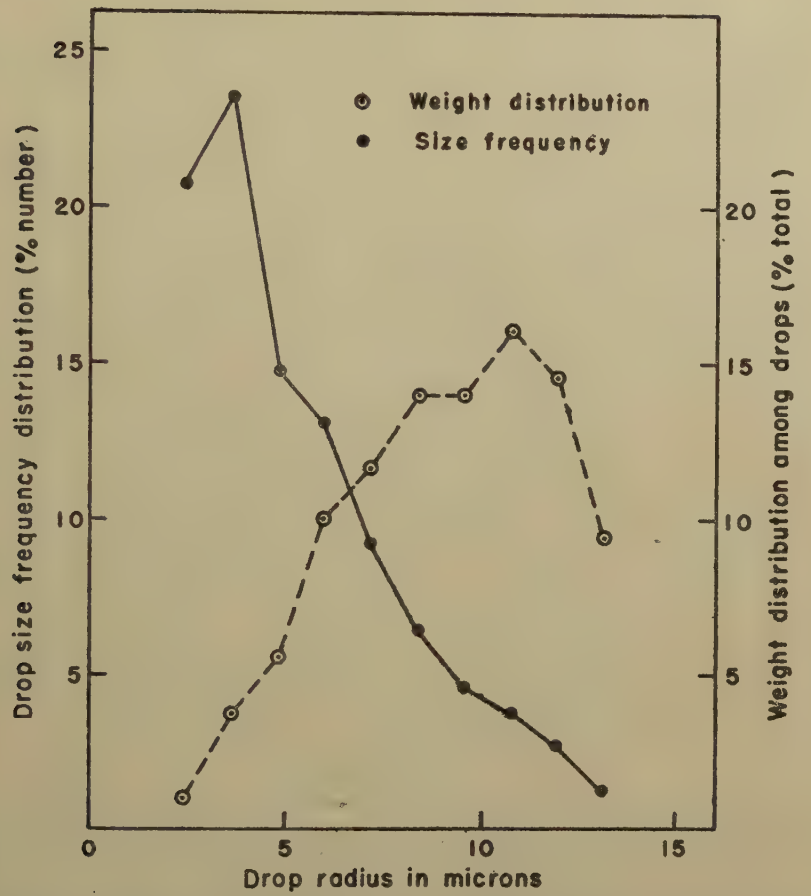

Figure 4. Approximate distribution of size and weight of sea water aerosols over Venice Beach, Fla., July 28, 1947. Sampling height 2 m, 50 m back from the edge of the sea. Wind velocity 4.2 m/sec south. Surf light.

respiratory irritation resulting from inhaling air from immediately over the various water samples.

In order to produce effervescence at room temperatures, a Pasteur-Chamberlain unglazed porcelain filter was placed in "red water," and air was forced through it under a pressure of 1.6 kg/cm^2. Clouds of fine bubbles were produced which, upon rising to the surface and bursting, formed a haze of drops in the air. Breathing this haze produced irritation of the nose and throat, though this effect was not as intense as that resulting from breathing vapor over effervescing heated "red

water." Similar tests with relatively clear sea water produced no irritation. The volume of sea water and "red water" used in these tests was about 2 liters and the water surface area exposed was about 200 cm^2.

When a pad of absorbent cotton 2 cm. thick was held over the mouth and nose, air inhaled from over effervescent "red water," heated or unheated, produced no irritation. This indicates that the irritant, as it exists in the air-borne form, can be reduced by filtration to a concentration which is not detectable when inhaled.

On the afternoon of July 28, 1947, the wind over Venice Beach shifted to the south (an onshore wind) and a slight throat irritation was noticed by the author and others. Glass slides (1 x 10 mm.) were exposed, normal to a measured flow of wind. Corrected counts (under a microscope) of the drops impinged upon these slides revealed a concentration of 112 drops per liter of air.[5] Fig. 4 shows the approximate size and weight distribution of the drops collected on a slide at this time. The weight of salt and water present was about 1.4×10^{-7} grams per liter of air. The method used in deriving these values is based in part upon the work of Houghton and Radford (1938), Langmuir (1944) and Langmuir and Blodgett (1945). An account of this method will be given in a later publication.

Unconcentrated "red water" containing 56×10^6 dinoflagellates per liter was stored for several weeks in well filled 19 liter bottles without preservatives. This water was found to retain its irritating qualities apparently unimpaired.

SUMMARY

1. Nose and throat irritations, similar to those naturally occurring in the Venice Beach region of the Gulf coast of Florida during July 1947, can be produced by breathing air artificially laden with small drops of the Gulf of Mexico water which contains (or contained) 56×10^6 dinoflagellates per liter.
2. The presence of naturally produced drops of sea water in the air along Venice Beach, Florida, during a time when respiratory irritation occurred, is indicated. Approximate drop size range and concentration is given.
3. Simple experiments show that respiratory irritation is always associated with the presence of small drops of "red water" in the air.
4. "Red water" stored without preservative for several weeks retained its irritating qualities apparently undiminished. The persistence of the irritant through weeks of storage without preservative and

[5] During heavy surf conditions, with onshore wind, concentrations as high as 3,000 drops per liter of air have been measured by the author.

through large temperature changes indicates a rather stable substance.

5. Drops from effervescing heated "red water" were more irritating than drops from effervescing water at room temperature, and these later drops seemed more irritating than spray drops produced by the hand atomizer.
6. The irritant passed through a fine bacteria filter (1 to 1.5 micron openings).
7. When air-borne, the irritant can be so reduced in concentration, by inhaling through absorbent cotton, that it ceases to affect the respiratory system.

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